SLOW-RELEASE FERTILIZER MATERIALS BASED ON MAGNESIUM AMMONIUM PHOSPHATE

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SLOW-RELEASE FERTILIZER MATERIALS BASED

ON MAGNESIUM AMMONIUM PHOSPHATE

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Project E-19-630 and I hope that he continues working with fertilizers. Dr. Cochran has also contributed to the project with his expertise on X-ray diffraction.

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SUMMARY

In a research project at Georgia Tech two new processes for the manufacture and use of magnesium ammonium phosphate based fertilizer mixtures were invented. The dissertation describes the course of the research from the conception of the processes, through the laboratory studies, to the pilot-plant production and agronomical use.

The first process described is one in which a finely divided dry feed consisting of a mixture of seawater magnesia, fertilizer grade monoammonium phosphate (MAP) and optionally other dry powders, fines, or micronutrient carriers, was granulated continuously in a pan granulator, with a fine water spray providing the liquid phase necessary for agglomeration. The water caused magnesia and MAP to react according to the following equation:

$$MgO + NH_4H_2PO_4 \rightarrow MgNH_4PO_4 \cdot H_2O$$

The reaction was not complete throughout the mass of the granules because the water of granulation was limited. Sufficient reaction took place, however, to insure a strong cementing of the finely divided feed in a hard, well-formed, round granule. The product was free-flowing, non-caking, non-smelling, and very dry. With respect to the previously reported methods for manufacturing magnesium ammonium phosphate, the new method has the intrinsic advantage of dispensing with drying and cooling and may be run with an extremely low recycle ratio. Also, the raw materials for the dry feed process are easy to store and to handle, contrary to the

raw materials for the slurry feed processes, which are hazardous and corrosive. Typical formulas produced were 8-32-0-11 ($N-P_2O_5-K_2O$-Mg) and 7-29-7-9. The N/P_2O_5 ratio varies according to the source of MAP. Also, some ammonia may be lost when the MAP contains diammonium phosphate in a substantial amount.

The fact that the reaction was not complete is not a disadvantage. It was postulated that the reaction continues in situ, i.e., after the moisture from the soil penetrates the granules. This hypothesis was confirmed by the leaching patterns obtained for the product, indicating good slow-release characteristics. X-ray diffraction patterns obtained for typical pilot-plant products, for leaching residues and for dried products, also confirmed that hypothesis, besides giving other valuable insight into the process and into the behavior of the product. For example, when water of granulation was 20% of the total feed, approximately 45% of the reactants reacted to form $MgNH_4PO_4 \cdot 6H_2O$. The -8+12 mesh fraction of the product had 13% of the N and 11% of the P rapidly leachable. For an equivalent granule size of MAP, 64% of the N and 54% of the P were readily leached, under the same conditions in a certain leaching column.

The second method described is a slurry application. The slurry was produced by the reaction of either granular or powder MAP with sea water magnesia, inside the tank of a hydromulcher, at the site to be planted or fertilized. Readily available intermediate materials were thus reacted to form a product which consisted of a soluble part (20%) and an insoluble part (80%). X-ray examination indicated that the insoluble part consisted mainly of $MgNH_4PO_4 \cdot 6H_2O$. When KCl was added, formation of $MgKPO_4 \cdot 6H_2O$ was observed. It was found that nutrients in the slurry,

including the soluble part, were released slower than from granular MAP, when subjected to similar leaching conditions.

Uses for both experimental products are suggested. Several agronomical experiments were conducted, mainly on roadside plantings, but results were not yet conclusive at the present time.

GLOSSARY

MAP - Monoammonium phosphate. Because of varying grades of phosphate rock and levels of impurities in phosphoric acid, the P_2O_5 content in MAP varies. Its usual range goes from 48% to 55%. The N content usually varies from 10% to 13%. Thus, contrary to DAP (diammonium phosphate), which is 18-46-0 ($N-P_2O_5-K_2O$), MAP does not have an established grade. Ordinarily available in granular form, it was recently made also available in a powdered form (10-50-0).

DAP - Diammonium phosphate; fertilizer grade 18-46-0. It is a mixture of diammonium phosphate and monoammonium phosphate in a 4:1 molar ratio, plus impurities. A number of years ago, 16-48-0 was also called DAP.

MAGAMP - Tradename for a magnesium ammonium phosphate and magnesium potassium phosphate product from W. R. Grace & Co. Typical analysis is 6-28-6-8 ($N-P_2O_5-K_2O-Mg$).

MAGOX 98 HR - A highly reactive sea water magnesia used as raw material for MNP, MNPK, and HYDROMIX.

MNP - Name coined for a new granular slow-release fertilizer based on magnesium ammonium phosphate being developed at Georgia Tech. Typical analysis is 8-32-0-11. Grade may vary with the grade of raw material MAP.

MNPK - Similar to MNP, with the addition of K_2O values. Typical analysis is 7-28-7-9.

HYDROMIX - A slurry fertilizer being developed at Georgia Tech. The slurry is slow-release and is based on magnesium ammonium phosphate.

CHAPTER I

INTRODUCTION

This thesis is concerned with what is called, at the Georgia Institute of Technology, "Project E-19-630." This project was initiated on July, 1974, being sponsored by the Georgia Institute of Genetics. This thesis describes most of the work performed from that date up to December 1976. It omits most of the agronomical testing, which is not yet conclusive.

Dr. G. L. Bridger, project chairman, and Director of the School of Chemical Engineering at Georgia Tech, while with W. R. Grace & Company, did pioneering work with magnesium ammonium phosphate. New ideas for the granulation of this fertilizer material and the emergence of new applications for fertilizer slurries have brought Dr. Bridger to propose the development of new methods of production and use of magnesium ammonium phosphate based fertilizers. Early in 1974, Dr. Bridger wrote a proposal entitled "Multi-purpose Time-release Fertilizers" (1). In the introduction of that paper he stated:

> Effective and economical application of fertilizer nutrients is a complex engineering problem due to the wide variation of soils, climate and vegetation locally. Many soils in Georgia present substantial deficiencies in plant nutrients while the abundant rainfall and water run-off tend to remove any available nutrients rapidly. This program has been formulated to develop some new approaches toward improving the economics of fertilizer application and enhancing the long-term effectiveness of the plant nutrients.

It would be difficult to be more clear and concise about the objectives

of Project E-19-630. Following the introduction, Dr. Bridger outlined the tasks to be taken, in order to develop, step by step, the research project. Although some unexpected results have led us to change some routes, the basic concept of the project was not changed.

Generalities

Fertilizer is a main component of the cost in most farm and in many non-farm plantings. Due to a growing world demand, together with the limitation of raw materials supply, the importance of fertilizer as a component of the cost in plantings is expected to increase. Growing awareness of the fact that the reserves of minerals and fossil fuels are limited has directed a good part of the fertilizer research in the last two decades toward the development of more efficient sources of plant nutrients or toward finding ways to improve the efficiency of known sources. Because of the intricate fertilizer-soil-plant relations, this development has had multiple aspects. One important aspect has been the study of less soluble materials as nutrient sources. Because ordinary materials are soluble, a significant fraction of the nutrients may be leached very rapidly from the soil. It is not the purpose of this paper to discuss the nature and the extent of such losses. This is a complicated problem and several agronomical papers would be more adequate as reference (2,3). Here the discussion is limited to mentioning that several losses are related to the high solubility of fertilizer materials. Burning of seeds, roots, or leaves, low efficiency in phosphorus assimilation, losses by nitrification-denitrification sequences, leaching and short-term fertilization effects make a highly soluble form of fertilizer inadequate for a number of uses or for some methods of application.

Magnesium ammonium phosphate is a rather insoluble compound and thus has been considered for a long time as a fertilizer whenever slow-release, non-burning characteristics are desired.

Objectives of the Research and Development

This research project was centered on the development of two processes in which magnesium ammonium phosphate is the base component. In one process, the product is granular; in the other, it is a slurry. The objectives of the research and development were to define the processes, characterize the products, to verify their uniqueness and originality, to examine the economies brought by their development, and investigate their agronomical performances. All objectives were realized, but agronomical evaluations are slow and cannot be considered so far conclusive. Therefore, final results are not present in this thesis; however, uses for the products are suggested and discussed.

In Chapter II the literature on magnesium ammonium phosphate is reviewed. The main methods of fabrication are examined and the basic features of the two new processes are outlined. It is also made clear why the new processes should be competitive with the existing proposed methods.

In Chapter III the actual development of the granulation process is described. A pilot-plant scale pan granulator was built and the operation is described. Some art was necessary to "make the process work." The product was characterized as a trouble-free fertilizer material, in fact with very good physical properties. The resistance of the products against leaching was determined relatively to a soluble control and to an insoluble control. The soluble control was fertilizer grade MAP and

the insoluble control was MAGAMP. X-ray diffraction analyses characterized several typical products, leaching residues and dried material, lending valuable insight into several phenomena observed in the course of the research. The process and products are discussed at the end of the chapter, and some uses are suggested.

Chapter IV is devoted to the slurry process and to the slurry product in more or less the same way Chapter III is to the granulation process and product.

Agronomical testings are described in the next chapter, and in the final chapter a set of conclusions and recommendations is put forward.

Precise details on testing equipment and on analytical work can be found in the appendices. It was chosen to present the analytical methods used, since non-official methods and modifications of official methods were adopted. This was so done because the analyses of hundreds of leachates, each with respect to several components, required faster, more economical methods.

The text is referenced by a numbering system to a list of references. On a parallel basis, when a source is mentioned in the text with a date, such as Smith (1949), it should be referred to the Selected Bibliography on Magnesium Ammonium Phosphate.

In this introduction a final paragraph or two are necessary in order to explain the scope and the objectives of the agronomical testing. Although laboratory experiments can give indication as to how good a non-burning, slow-release fertilizer is, such results cannot be extrapolated to field conditions. Obviously a fertilizer is only as good as shown by its agronomical performance. Due to the large number of variables to be

controlled in an agronomical test, field evaluation of fertilizers requires much expertise. Due to the complementary role of nutrients, their sources and rates, seeding rates and variety, soil status and management, climate, machine and human factors, agronomical trials must usually be very numerous in order to be significant. The agronomical tests conducted in this project have the objective of proving simple hypotheses, that the fertilizers invented perform better than the ordinary materials presently used by the State of Georgia in its highway plantings. The program adopted, if successful, would immediately benefit the State, in particular its highway maintenance work. The granular material was thought particularly suitable for the tree and shrub planting programs and the slurry method adequate for new grassing and refertilization projects. Potentially, both products have broader uses. The fact that both processes yield fertilizers with an immediately available part and an insoluble, slow-release part is an advantage over both completely soluble and completely insoluble fertilizers.

CHAPTER II

MAGNESIUM AMMONIUM PHOSPHATE: LITERATURE SURVEY

Generalities

Magnesium ammonium phosphate is a compound of the formula $MgNH_4PO_4 \cdot nH_2O$. In nature, it exists ordinarily as an hexahydrate. It has the unusual feature that all its elements are necessary plant nutrients. Like all metal ammonium phosphates, it is quite insoluble in water, hence its potential use as a long-lasting, non-burning, slow-release fertilizer.

Ample experimental evidence is available to rate magnesium ammonium phosphate as an efficient source of magnesium, nitrogen and phosphorus (4). Because of its low solubility it is a non-burning material (5); when finely divided, (e.g., in a slurry) it may be efficiently used in foliar application (6). It was found that its breakdown in soil, as measured by the rate of nitrification, was much faster than solubility could explain, and that microbiological attack was the rate setting factor. A subject of patents was the discovery that granulation could control the microbiological breakdown. Therefore, as a granule, magnesium ammonium phosphate can be expected to be a long-lasting fertilizer (7). Its main disadvantage as a source of nitrogen is its low N/P_2O_5 ratio.

The literature on magnesium ammonium phosphate is quite rich. Methods for its production as a fertilizer have been the subject of many patents. A number of other patents list magnesium ammonium phosphate

either as a co-product or as a by-product. Many fundamental chemistry studies on magnesium ammonium phosphate are available. This is partly due to its importance in quantitative analysis of magnesium, and also because it occurs widely in ammoniated fertilizers. It is worth mentioning that magnesium ammonium phosphate has been identified as a product of reactions of ammonium phosphates with soil (8). For many years it has been the subject of a sizable volume of agronomical testing. It is useful to view its fertilizer related literature in perspective. Table 1 summarizes this view.

Table 1. The Importance of Magnesium Ammonium Phosphate in the Fertilizer Literature[a]

	Number of Articles		
	Up to 1950	1951-1965	1966-1976
Methods	4	6	17
Use	5	22	12
Fundamentals	1	2	6
Reviews	-	-	5

[a]Compilation based on a TVA-NFDC Bibliography (9), on the work of Bridger (1968) and on manual searches.

Note that the appearance of magnesium ammonium phosphate in reviews is to a great extent due to the interest in slow-release fertilizers observed since the last decade. Similarly, a review on magnesium fertilizers may have been included in that category. Therefore, some variation in the numbers presented in Table 1 may exist, due to classification of the articles. Also, it is very possible that some work may

have passed undetected. The point is to show that magnesium ammonium phosphate has awakened a large interest. However, the reality is that it has been produced commercially in this country only on a very limited basis. It is assumed that expensive manufacturing is one main cause for that fact.

In this dissertation the literature review will be limited to the main existing methods of production, i.e., those the new proposed methods would have to compete with. Basic features of the two new methods are then given and discussed.

Granulation Methods

Methods Reported in the Literature

Almost all magnesium ammonium phosphate processes intended for fertilizer production yield solids, either granulated or powdered. In both cases, usually a slurry is produced, which is then either settled and the solids dried or granulated.

Almost all granulation methods reported are slurry granulation methods, i.e., those in which a wet feed coats dry recycle inside some granulation equipment. Usually the recycle ratio is high and so is the moisture to be driven off the product. In the preparation of the slurry feed for granulating magnesium ammonium phosphate, for all practical purposes the choice of raw materials has been restricted to combinations of the following: anhydrous ammonia, nitrogen solutions, urea, for the nitrogen; phosphoric acid solutions, for the phosphate; and magnesia, magnesium hydroxide, carbonate, silicates, sulfates, dolomites and other sources for the magnesium. It is easily visualized that any combination

of such feeds would have to be slurrified for their contact to be intimate enough in order to obtain a complete reaction.

Besides the choice of feed, there is some variation in the equipment used. In general, there is a combination of a preneutralizer, or a slurry reaction tank, a pugmill mixer and the drum ammoniator-granulator. Some methods require heating; for example, those in which urea is the source of ammonia. Finally, there are variations in the order of addition of the feeds, in other words, in the way the pH changes as the process proceeds.

A general slurry feed preparation could be taken as that described in the patent due to Salutsky, Lee and Bridger (1964). Simplified, the preparation method has two steps. In the first step, a finely ground suitable magnesium compound is slurrified and reacted with phosphoric acid under heat (175-225°F) and vigorous agitation. The pH after digestion ranges from 4.0 to 6.0. The reaction is postulated to be:

$$MgO + H_3PO_4 + 2H_2O \rightarrow MgHPO_4 \cdot 3H_2O \qquad (II-1)$$

This dimagnesium phosphate slurry is then ammoniated to pH 7-8 by allowing ammonia to bubble-in while maintaining a temperature of about 190°F. The neutralization proceeds according to the following equation:

$$MgHPO_4 \cdot 3H_2O + NH_4OH \rightarrow MgNH_4PO_4 + 4H_2O \qquad (II-2)$$

The preparation is expensive, although suitable to a wide range of magnesium sources. Under normal conditions of preparation, the magnesium ammonium phosphate would be an hexahydrate.

With small variations, other methods are similar to the above

described one. As a rule, they were developed to make use of some particularly available feed. Thus, Varshavsky et al. (1969) use a phosphoric acid extracted from a phosphorite containing a high level of magnesium; Taborsky et al. (1974) use a waste phosphoric acid; Kowalsky and Bodzek (1970) utilize wastes from a magnesite mine. Similar applications were developed by Kim (1972), Loeblich (1970) and by Mazaeva (1969).

The magnesium ammonium phosphate prepared according to any of the mentioned methods would be a feed for the granulation method patented by Bridger and Alfrey (1964). That was the first application of the observation that the breakdown of magnesium ammonium phosphate in soils was controlled by the microbiological attack, and that granulation could control this attack. In that process, a 70% water, 30% $MgNH_4PO_4 \cdot H_2O$ slurry was fed in a rotary drum, onto a bed of dry recycle. The $MgNH_4PO_4$ in the slurry feed and in the recycle were reported to be in a 1:1 ratio. It is easily observed that a considerable amount of drying was necessary. Also, the granules were not particularly strong, although it was claimed that the granule strength increased after application to the soil.

A departure from the first granulation process was offered by Hudson (1969). A slurry process was described in which anhydrous ammonia and a phosphoric acid solution in stoichiometric amounts to form monoammonium phosphate were sparged underneath a bed of recycled solids, while a 35% solids magnesium hydroxide slurry was sparged on the top of the rolling bed. Thus successive layers of monoammonium phosphate and magnesium hydroxide coated the recycle; reaction between the layers yielded magnesium ammonium phosphate. Alternatively, the $Mg(OH)_2$ slurry could be fed in a second section of the drum, separate from that in which acid and

ammonia react. The recommended recycle ratio was 4:1. A large drying requirement was supposedly present.

In the original MAGAMP process, Legal and Mobley (1967) granulate a $Mg(OH)_2$ slurry (46% solids), acidified and ammoniated in a pugmill, with recycle product, to give a 7-9% N, 42-45% P_2O_5 magnesium fertilizer. Drying and cooling were necessary. The recycle ratio was not disclosed. That process was extended by Legal and Schindler (1968) to produce a magnesium ammonium phosphate and magnesium potassium phosphate fertilizer. The inventors used a nitrogen solution (43% urea, 30% NH_3), mixed thoroughly with a $Mg(OH)_2$ slurry and had the mixture fed at the front end of a pugmill. Downstream from the pugmill, enter H_3PO_4 and then a KOH solution. Very hard, slow-release granules were obtained after drying and cooling. The role of urea in the manufacture of magnesium ammonium phosphate is described by the equation:

$$(NH_2)_2CO + 2H_3PO_4 + 2MgO \rightarrow 2MgNH_4PO_4 + H_2O + CO_2 \qquad (II-3)$$

In the Legal and Schindler process, however, urea apparently played a major role in obtaining very strong granules. Yoshita (1971) in a similar way describes a process in which urea alone is the source of nitrogen.

Significantly different from slurry feed processes are the dry feed processes. Since MAP became available as a commercial fertilizer, it has been naturally considered for a number of processes where originally ammonia and phosphoric acid were the reactants. The main advantages of using MAP are in the storage and handling operations. While acid and ammonia are corrosive and hazardous, MAP is a trouble-free granular solid. Even with powdered MAP, dust is not an uncontrollable problem. MAP and

magnesia, in the presence of water, react according to the equation:

$$MgO + NH_4H_2PO_4 \rightarrow MgNH_4PO_4 + H_2O \qquad (II-4)$$

Thus, upon availability of MAP, new processes for the manufacture of magnesium ammonium phosphate have appeared.

Kawamoto and Kubota (1971) and Stevenson (1968) described processes based on reaction (II-4). Both used premixed powdered dry feed. The first process used $Mg(OH)_2$ and $NH_4H_2PO_4$, granulating in a rotary drum, with water and steam. Preheating the dry mix was recommended and a granular $MgNH_4PO_4$ product was claimed. In the other process, a fine sea water magnesia and crystalline monoammonium phosphate mixture was granulated in a pan granulator, "with sufficient water to effect granulation." The operation was batchwise and the products were dried and cooled. After the first pass, the fines and crushed oversize were repassed and then a 90% granulation efficiency was claimed.

It is worth mentioning other processes which make use of reaction (II-4), although $MgNH_4PO_4$ is not the main product of the process. Akiyama and Takaoka (1971) described the granulation of a $Mg(OH)_2$, MAP, urea and K_2SO_4 mixture. Only 10% water was necessary for good granulation. $MgNH_4PO_4$ was present in the product. Christoffel and Strother (1968) described a process in which urea granules were wetted with phosphoric acid and subsequently dusted with diammonium phosphate and magnesia powders. The reactions were:

$$H_3PO_4 + (NH_4)_2HPO_4 \rightarrow 2NH_4H_2PO_4 \qquad (II-5)$$

$$2NH_4H_2PO_4 + 2MgO \rightarrow 2MgNH_4PO_4 + 2H_2O \qquad (II-6)$$

A slow-release nitrogen fertilizer, a "magnesium phosphate and magnesium ammonium phosphate coated urea," was claimed. Ushioda et al. (1973) described a similar process, and it was claimed that the coating controlled nitrification, with or without the addition of nitrification inhibitors.

The Georgia Tech Process

A process has been developed in which a finely pulverized mixture consisting of sea water magnesia and MAP in stoichiometric amounts to form magnesium ammonium phosphate was fed and granulated continuously in a pan granulator, with a fine water spray providing the liquid phase necessary for agglomeration. Fine KCl, as well as other powders or fines could be incorporated in the granules. Sufficient crystalline phase consisting of $MgNH_4PO_4 \cdot 6H_2O$ was present to assure the formation of a strong granule, but not enough water was provided for the reaction to be complete. Conversion of the reactants was less than 50% in processing. When the fertilizer is used, at least part of the remaining reactants will continue to react in situ, when soil moisture penetrates the granules. The product dispensed drying and cooling, required no heat to be formed and pilot plant experience indicated that manufacturing this product in a well-operated industrial pan granulator may require only a very low recycle ratio. The product could be dried after curing, if so desired, and still retain its hardness and strength. Typical formulas produced were 8-32-0-11 ($N-P_2O_5-K_2O-Mg$) and 7-29-7-9. The N/P_2O_5 ratio would vary with the source of MAP used.

The Georgia Tech process is fundamentally different from the slurry feed, wet granulation process. Advantages in handling and storage are

clear; MAP is a trouble-free solid, while ammonia and phosphoric acid are hazardous, corrosive and require special handling and storage. Also, ammonia feeds usually imply a need for scrubbing operations. The drying and cooling operations inherent to slurry granulation also usually imply scrubbing and dust collection, all of which are energy-intensive steps.

Without any doubt, this new dry feed process touches some of the points of the Kawamoto and Kubota (1971) and of the Stevenson (1968) processes. It can be differentiated from the first by the pan granulation and by the partial reaction in plant and completion after application to the soil. The Stevenson process, however, makes use of the pan granulator. Perhaps two main differences could be found between that process and the Georgia Tech process. First, in the Georgia Tech process most of the reactants remain unconverted after the manufacturing step, while the Stevenson process claims a method for manufacturing magnesium ammonium phosphate. Second, Stevenson described a process in which the amount of water is not specified, and the product required drying, whereas in the Georgia Tech process the water for granulation was carefully controlled so that no drying was required.

Slurry Methods

The use of magnesium ammonium phosphate in a slurry form was proposed by Bridger and McCullough (1961). In the main version of that method a slurry was manufactured by the agitation of a MgO-DAP mixture in water. The reaction gave a $MgNH_4PO_4$ precipitate, at the same time forming ammonium hydroxide:

$$MgO + (NH_4)_2HPO_4 \rightarrow MgNH_4PO_4 + NH_4OH \qquad (II-7)$$

The resulting slurry presented a concentration of about 1.3 lb of solids per gallon, the pH was around 8 and the conversion of reaction (II-7) was measured to be 40%. The conversion was computed from insoluble nitrogen analyses. Presence of KCl and urea did not reportedly affect the conversion. The slurry was claimed as a long-lasting, non-burning fertilizer, almost twice more efficient than a conventional slurry (made from ordinary soluble fertilizer), when used in lawn applications.

At the time of Bridger and McCullough's work (1961) MAP was not commercially available. With the present availability of such raw material it was logical to develop a process in which MAP and MgO are the reactants to form a magnesium ammonium phosphate slurry. Advantages over the DAP-MgO mixture are more insoluble nitrogen, less ionic concentrations in the slurry and negligible ammonia losses. Moreover, MAP is also produced in powdered form. This actually microgranular form constitutes the ideal raw material for a magnesium ammonium phosphate slurry process, allowing possibly substantial reductions in operating costs. At Georgia Tech the new slurry application was developed aiming at the grassing operations along highways. This operation is usually done with hydroseeders, permitting the seeding, mulching and the fertilization to be combined in one operation. According to reaction (II-4), magnesium ammonium phosphate was obtained when a sea water magnesia and MAP mixture was reacted inside the tank of a commercial hydroseeder, in which rotating blades and/or a recirculating pump provide strong agitation. Thus a non-burning, slow-release fertilizer can be produced from readily available, low-priced intermediates, with a minimum of extra operations (See Figure 12).

The use of magnesium ammonium phosphate as a fertilizer in a fluid

form has not received much attention, although a potentially vast range of applications exist. While keeping essentially all the advantages of fluid fertilizers, it can also be safely applied in foliar applications and may be used at higher rates.

CHAPTER III

GRANULATION PROCESS FOR THE MANUFACTURING OF MAGNESIUM AMMONIUM PHOSPHATE BASED FERTILIZERS

A method for granulating a finely pulverized uniform mixture, consisting of sea water magnetia and MAP, with possible incorporation of other powders or fines, was developed. Continuous production in a pan granulator was attained, with a fine water spray providing the liquid phase necessary for agglomeration. The resulting granules did not require drying or cooling, and exhibited excellent physical properties. The products were named MNP and MNPK, to indicate granular mixtures containing magnesium, nitrogen, phosphorus and also potassium. Typical grades were 8-32-0-11 ($N-P_2O_5-K_2O-Mg$) and 7-29-7-9. The actual grade may vary with the grade of MAP used. Higher grades may be obtained by drying.

Pilot-Plant Production

A mini-pilot plant was constructed to produce the MNP and MNPK materials. It consisted of a 24-inch diameter pan granulator, equipped with variable speed of rotation, variable inclination, and variable bed depth. Feeding was provided and controlled through vibratory feeders. A fine water spray feed was obtained by means of reduced line pressure and a hydraulic nozzle. Photographs showing overall and detailed views of the pilot-plant are presented in Figures 1-3.

Raw Materials

The magnesium source used in the process was sea water magnesia.

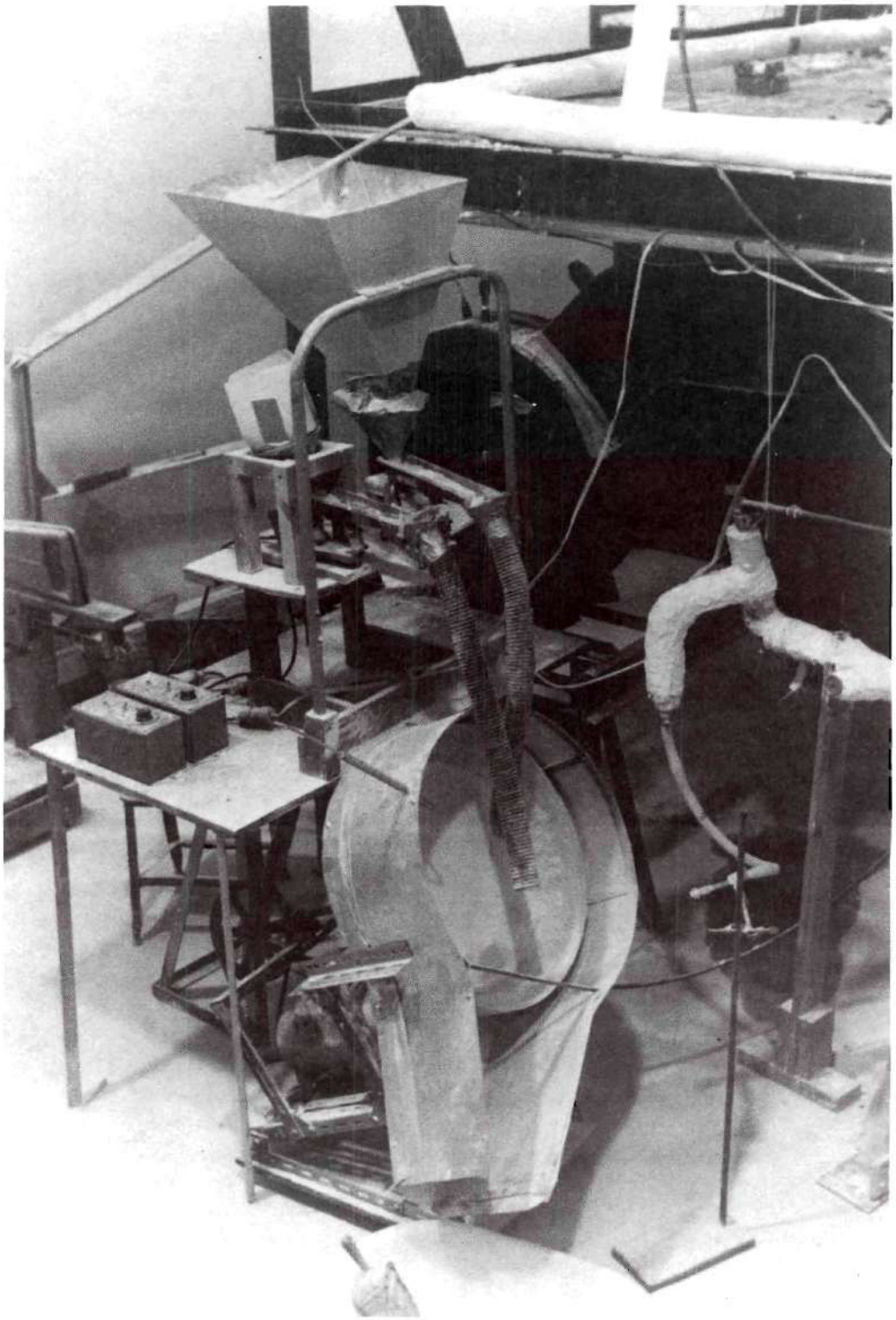

Figure 1. Overall Picture of Pan Granulation Mini Pilot-Plant.

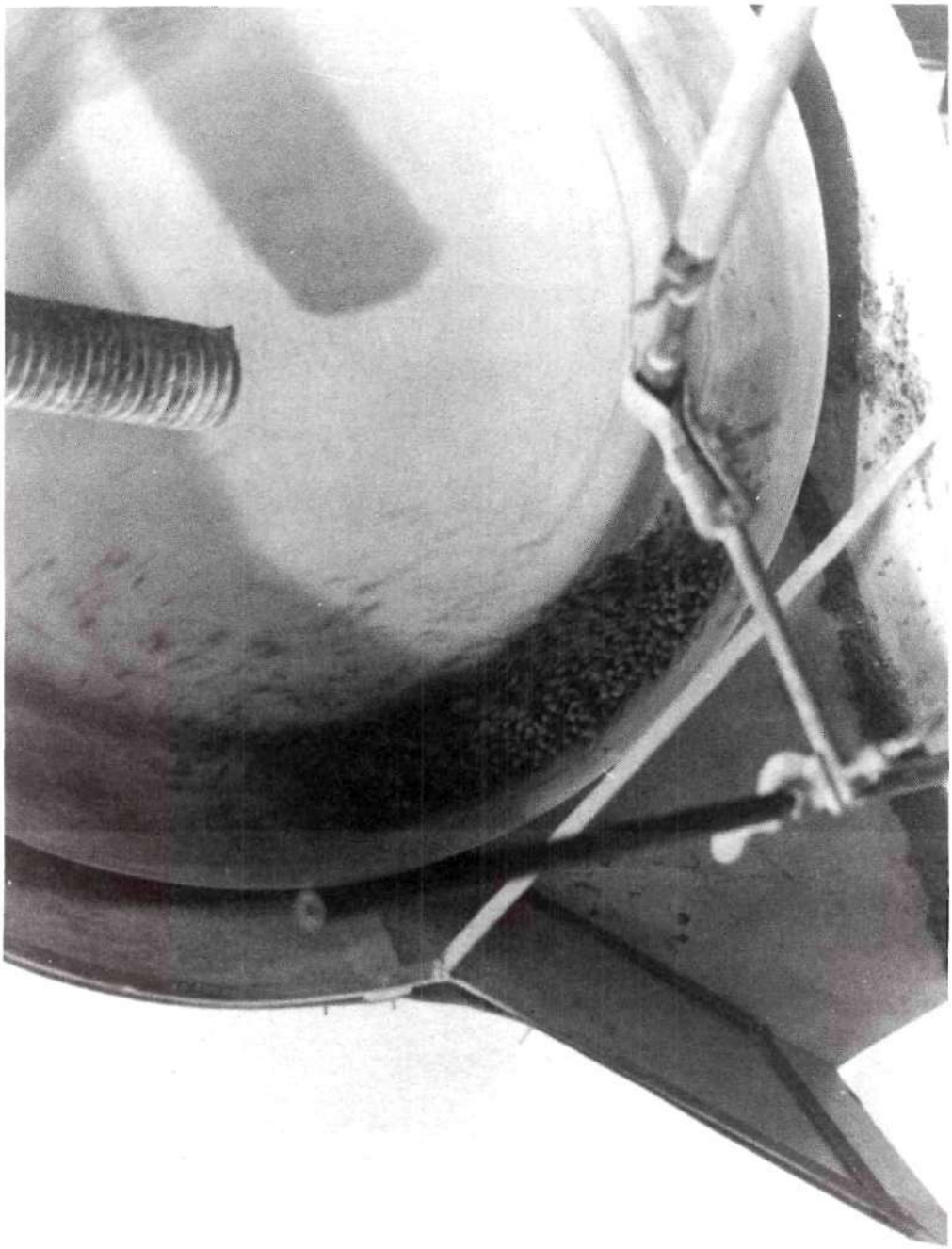

Figure 2. Detail of Operation: Sizing Action in Pan Can Be Observed.

Figure 3. Operation of the Pan Granulator Required Careful Placement of the Feeds.

This is a highly reactive magnesia, precipitated from sea water and calcined at low temperature. It was supplied by Basic Chemicals, Inc., from Cleveland, Ohio, and produced in Port St. Joe, Florida. The type used was Magox 98 HR, 98% -200 mesh.

Two MAP's were used, a 13-52-0 and a 11-52-0. Both were granular (-6+16 mesh) fertilizer grade materials. The 13-52-0 was supplied and manufactured by Gardinier, from Florida; and the 11-52-0 was supplied and manufactured by Agrico, from Donaldsonville, Louisiana.

The KCl used was soluble grade, 62% K_2O, -20 mesh crystals; and it was supplied by Fowler Fertilizers, from Lithonia, Georgia. A finely divided potassium sulfate (50% K_2O) was used when a chloride-free grade was produced. It was supplied by Pelham Phosphate Company, from Pelham, Georgia.

Micronutrients were obtained from Traylor Company from Orlando, Florida, and were all sulfates, except for the ammonium molybdate and for the borate. All micronutrients were in the form of fine powders. For example, the following formulation was used in the main production run:

MgO (sea water magnesia)	400 pounds
MAP (11-52-0)	1,200 pounds
K_2SO_4 (0-0-50)	264 pounds
$MnSO_4$	30 pounds
$CuSO_4 \cdot 5H_2O$	30 pounds
Sodium Borate	10 pounds
$FeSO_4 \cdot 7H_2O$	40 pounds
$ZnSO_4$	30 pounds

Ammonium Molybdate	2 pounds
Total	2,006 pounds

The dry mix grade was 6.6-31.2-6.6-11Mg-7S-0.37Cu-0.1B-0.4Fe-0.4Mn-0.54Zn-0.05Mo. To this formulation, 25% water was added for granulation.

The critical proportion in the formulation was the 1:3 MgO:MAP ratio. A lower ratio would not accomplish the purpose of insolubilization of MAP's nutrients; a higher ratio would yield magnesium phosphates, with release of ammonia.

Preparation of the Feed

A mix-muller was used to pulverize the MAP granules to a desired fineness. Several grades of fineness for the MAP feed were tried. Other raw materials did not require grinding. Table 2 describes the particle size of several dry feeds.

The dry powders were mixed in definite proportions in a closed drum set on rollers. In about 5 minutes an uniform mixture was produced. Premixing of the dry feed was essential for the granulation. It is not recommended in this process to feed the components separately. The feed hopper was then charged with the dry mix, while seeding granules (-16+32 mesh), collected from previous runs, were charged to a smaller "recycle" hopper. The arrangement is shown in Figure 1. It must be noted that this was not a true recycle. The purpose of this feed was to provide seeds for granulation and to help control production. It was used according to judgment of the operator, and in some instances it was possible to continue production without this feed for relatively long periods.

Operation of the Pan

Some art was necessary for attaining satisfactory production.

Table 2. Particle Size Distribution of Feeds and Effect on Granulation.

Feed Materials	% Retained in Screen (Mesh Sizes)							Observations
	42	65	80	100	150	200	325	
Magox 98HR	-	-	-	-	-	-	2	
KCl (sol.)	10	35	60	90	93	-	-	
MAP Powders:								
Extracoarse	92	93	94	-	96	98	-	Unsatisfactory Granulation
Coarse	60	-	80	82	87	89	-	Unsatisfactory Granulation
Medium	20	-	45	54	60	70	-	Unsatisfactory Granulation
Fine	2	17	25	-	44	55	-	Satisfactory
Extrafine	-	-	-	2	10	22	55	Best, but Dusty

Rotation speed, angle with horizontal, bed depth, solid and liquid feeds rates and placement were all critical for the granulation. A proper rotation speed was necessary to produce a rolling bed of granules in the pan. The angle with the horizontal has to do with the same effect. Moisture of the bed and positon of the scrapper are also critical for the proper bed condition. Due to the small dimensions of the equipment, any change in the operating conditions very quickly caused imbalances in the granulation, setting the process out of control. Figure 4 describes the placement of the feeds. Because the pan granulator provides a sizing

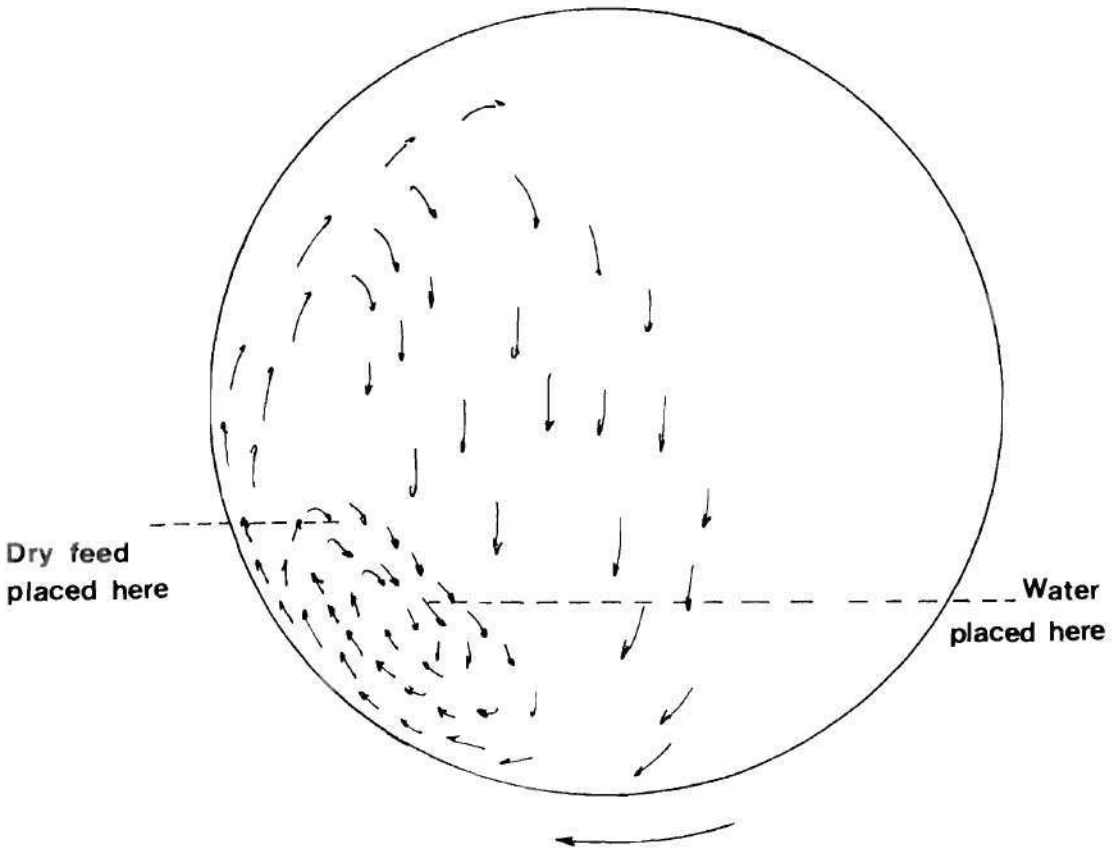

Figure 4. Schematic Description of Placement of Feeds on Rolling Bed of Granules in Pan Granulator.

action, some of which can be seen in Figures 2 and 3, it was possible to place the water spray over a section of the rolling bed of solids where growth of granules was desirable. The dry feed was placed in such a way as to coat just recently wetted granules. Typical operating conditions for the pan are listed in Table 3.

Table 3. Summary of Operation Data for the Pan Granulator

Diameter of the Pan: 24 inches
Depth of the Pan: 4 inches
Angle with Horizontal: 65°
Speed of Rotation: 36 rpm
Solid Feed Rate: 90 grams per minute
Liquid Feed Rate: 30 cm^3 per minute
Approximate area of Rolling Bed of Granules: 60 in^2
Approximate area covered by spray water: 18 in^2
Approximate area in which dry feed is placed: 3 in^2
Approximate Retention Time: 5 minutes
Temperature of the Bed: 50-60 °C

Finally, it must be noted that, as happens with granulation of fine powders and with the operation of the pan granulator, some art was necessary. The operation of the pan has been described in the above text, figures and Table 3. However, the author believes that the overwhelmingly critical factor in the manufacturing of the granules by the process described is experience of the operator, the ability to "read" the bed, in order

to make the proper adjustments in order to keep the process balanced.

Around 1000 pounds of material was produced. A wide range of granule sizes was produced for laboratory and field testing. Figure 5 shows the well formed, round granules.

Observations

Other observations were judged important and recorded below.

On the Feed. As typical with fine powders, the feed bridged while in the hopper, causing some difficulty in the feeding. Segregation of components in the hopper was not observable. Also characteristic of fine powders was dusting. One of the roles of water was to keep the dust in the process; it was found that without the fines to react granulation was not possible. A third observation of the feed was its compactability, which made the feeding rate unstable in the vibrating (volumetric) feeders.

Effect of Particle Size of MAP on Granulation. In the granulation of the mixture under consideration, it was one of the objectives to effect granulation with the least amount of water possible. The hypothesis was that the finer the feed, the higher the water requirements for granulation; the coarser the feed, the lower such requirements. The advantages from the use of less feed water would be less drying and higher analysis. After much experimentation, however, the use of coarser MAP did not produce satisfactory granulation. The MgO tended to granulate separately from the MAP. Consequently, some excess MgO was present in some granules, causing a very noticeable ammonia odor and also the granules thus formed were very weak. Because the difference in density and particle size between the seawater magnesia and MAP was very large, segregation in the pan would be expected. It was therefore concluded that since the

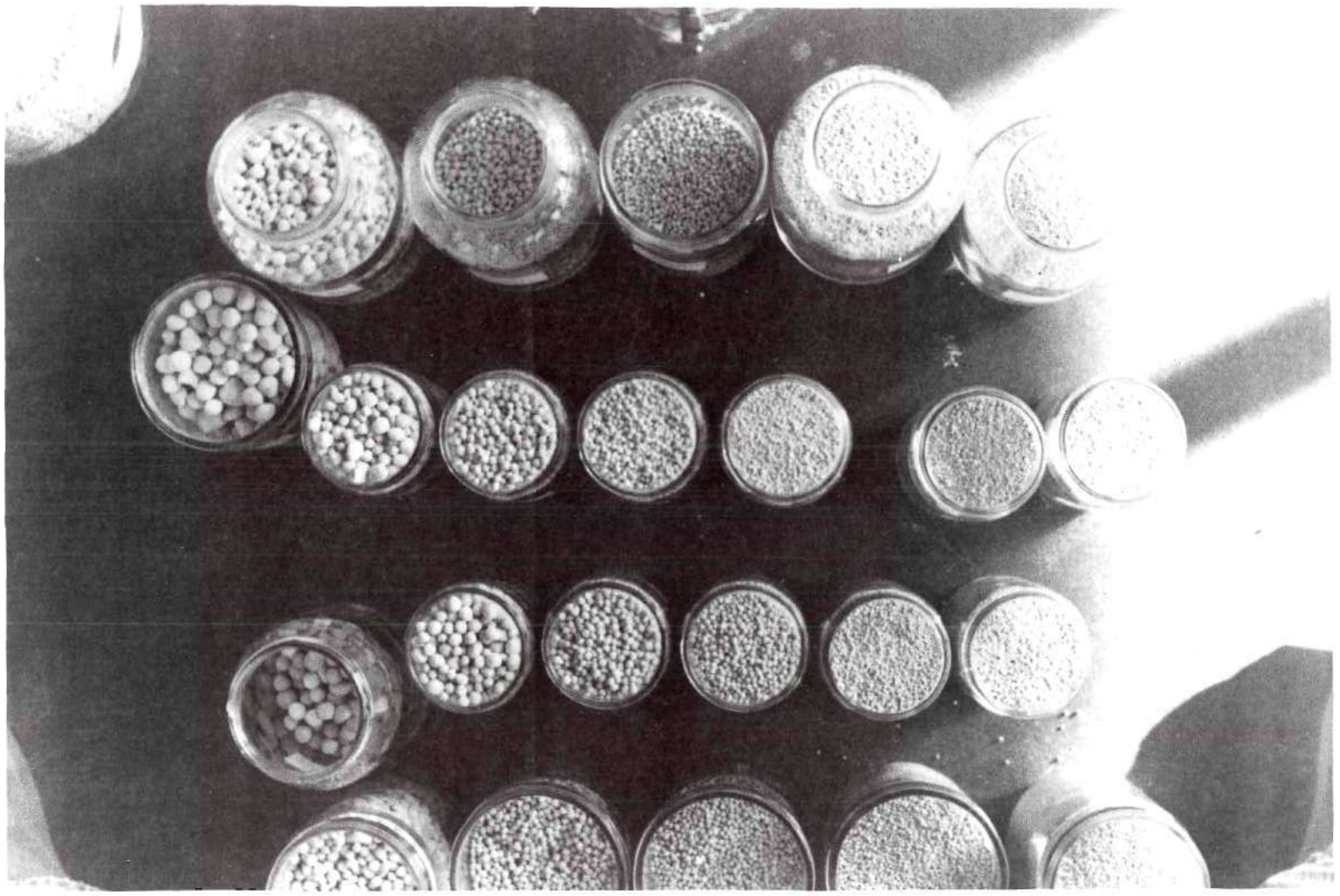

Figure 5. Final MNP and MNPK Products Were Strong and Well-Formed. Larger Granules are + 3/8", Smaller Ones are 0.02".

difference in density cannot be overcome, a close particle size distribution should be observed, in order to produce an intimate mixture of the reactants which would consequently rapidly produce the cementing reaction needed for the granulation. Because granulation is an art, however, it is possible that someone else succeeds in granulating a coarser MAP powder with sea water magnesia.

Water Content. Several reasons for minimizing the water requirements for granulation were already mentioned. Apparently, however, the amount of water required for good, efficient granulation was found to be fixed by the nature of the process. It was found that the water requirements would be in the following ranges:

To Granulate	Water Needed Was
MNP	25-30%
MNPK (with KCl)	20-25%
MNPK (with K_2SO_4)	25-30%

It would be possible to investigate granulation aids which would increase the liquid phase without increasing the water of granulation. It must be noted that granulation with about 15% water generated a dusty process and product; on the other hand, when too much water was present, the granulation bed would not roll adequately.

Efficiency of Granulation. Very low recycle ratios may be possible with this process. In the small pilot-plant equipment, very good granulation could be obtained. For example, in one run producing a MNPK fertilizer with KCl, from 10,871 grams of product, only 290 grams were -32 mesh. In another run in which MNPK was produced with K_2SO_4, in about 1,000 pounds of only 2.5% was -32 mesh, 24% was -16+32 mesh, and 66% was

-6 +16 mesh, the rest being +6 mesh. A more efficient granulation could be obtained in a larger equipment for the following reasons:

- More flexibility in the placement of feeds.
- More efficient use of the water for the granulation because of the larger bed of granules, which would allow more accurate placement.
- More defined sizing of granules in the bed, which would permit only on-size granules to leave the pan. Thus fines would be more efficiently thrown back into the granulation and imbalances in the process would be less likely to happen.

Ammonia Loss. Ammonia loss, as given by the change in N P_2O_5 ratio, was considered severe. As it was verified during the X-ray characterization studies, the ammonia losses can be assumed to be due mainly to the reaction of diammonium phosphate generally present in MAP:

$$(NH_4)_2HPO_4 + MgO \rightarrow MgNH_4PO_4 + NH_3 + H_2O \qquad \text{(III-1)}$$

The ammonia formed in the reaction could not be reabsorbed or fixed by the process solids. The losses correlated well with the percent weight loss at 105°C. That loss was proven to be water released in the transition

$$MgNH_4PO_4 \cdot 6H_2O \rightarrow MgNH_4PO_4 \cdot H_2O + 5H_2O \qquad \text{(III-2)}$$

This indicates that indeed ammonia was primarily lost in the reaction (III-1). The information contained in Table 4 reinforces that hypothesis.

The actual chemistry and stoichiometry involved in the losses of ammonia are rather complex. In Appendices D and E the reader will find

Table 4. Loss of Ammonia in MNP Granulation

Materials	N:P_2O_5	% NH_3 Loss (of Total N)	Moisture Content[a] (%)	Free Moisture[b] (%)	Conversion (%)
Feed (13-52-0)	1:4	-	1.5	1.5	--
MNP (+3/8")	1:4.55	10	21.0	2.17	35
MNP (-12+14 mesh)	1:4.9	18	25.0	1.31	40

[a]weight loss at 105 °C.

[b]Vacuum desicator method (10).

[c]See Appendix E.

longer discussions and calculations.

The observations described above give rise to the recommendation that the process utilizes MAP which would be virtually all monoammonium phosphate.

Segregation. No appreciable MgO-MAP separation was observed, except when a coarser MAP feed was used. Thus, P_2O_5 analyses, dry basis, were essentially the same, for the whole range of granules produced. It was observed, however, that different analyses per granule size could be related to different water contents. The segregation of water was understandable. Since smaller granules have a larger specific surface area, they received more of the water spray feed. For example, the data in Table 5 was typical.

In practice, segregation problems in granulation would disappear as recycle fines and crushed oversize return to the process. Equally,

Table 5. Segregation of Water According to Granule Size in MNP and MNPK Products

Particle Size (Mesh)	Percent Weight Loss		
	Run I	Run II	Run III
-3/8" + 4	21.4	19.8	20.2
-4 + 6	20.8	21.9	21.2
-6 + 8	21.4	23.0	22.4
-8 + 12	23.8	22.8	24.6
-12 + 14	-	25.0	-
-12 + 32	22.6	-	25.0

Particle Size (Mesh)	% Weight Loss	% P_2O_5	% P_2O_5, Dry Basis
-4 + 6	20.8	33.21	41.9
-6 + 8	23.0	31.26	40.6
-12 + 14	25.0	30.21	40.3

the segregation problem does not exist when the granulation is so efficient that all the feed is granulated.

Incorporation of KCl or K_2SO_4. In some runs, formulations were produced in which the K_2O content was the same as the N content. Because of much higher density and molecular weight, potassium salts at this level of content corresponded to only about 10% of the volume of the dry mixture. Therefore, incorporation of potassium salts in the granules did not change the granulation process. The pellets containing K_2O

values, either from KCl or from K_2SO_4, were harder, heavier, and somewhat easier to granulate than the potassiumless grade C. Those salts probably contributed to the liquid phase.

Incorporation of Micronutrients. In a special production run in which materials for testing in sand dunes were manufactured, micronutrients were required. The following finely pulverized micronutrient sources were used: $MNSO_4$, $ZnSO_4$, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, sodium tetraborate-pentaborate (20% B), and ammonium molybdate (54% Mo). Because the granulation efficiency was very high, it was assumed that the micronutrients were incorporated in the granules.

Strength of Granules. Just as they were produced from the pan-granulator, the granules were weak and tended to crumble at a firmer finger touch. However, they rapidly cured, and became eventually very hard. Table 6 shows the hardening of the granules.

Table 6. Crushing Strength of MNP and MNPK Granules, After and During Curing

Time (Hrs)	Crushing Strength, Lbs	
	MNP (-4+6 Mesh)	MNPK (-4+6 Mesh)
	0-1	0-1
1	1-3	1-3
3	1-3	2-4
16	2.5-4.5	3-5
72	4-7	6-8
96	6-7	6-9

Table 6 (Continued). Crushing Strength of MNP and MNPK Granules, After and During Curing

Granule Size (Mesh)	Crushing Strength		
	MNP	MNPK	MAGAMP
+4	8-16	8-16	14-22
-8+12	4-6	4-8	4-14
-12	2-3	2-3	3-4

Note: Typical prilled urea has crushing strength (-4+6 mesh) of 2 lb.

The hardness or strength of the granules were measured as the resistance to fracture of individual granules subjected to a force applied by a plunger (11). A small "kitchen balance" was used to measure the fracture force. It was observed also that potassium salts added to the strength of the granules, and that larger granules were stronger than smaller granules, due to the extra tumbling and rolling in the pan, which the larger granules, supposedly with a longer residence time in the pan, had to sustain.

Curing. The strength of the granules were related to aging and curing. While the granules immediately after leaving the pan were noticeably wet, cured granules were very dry. In fact, very little free water remained in the granules after curing. The temperature of the granulation bed explains the phenomenon. The temperature of the bed was around 60 °C due to the heat of reaction. Magnesium ammonium phosphate hexahydrate is the stable form below 57 °C (Bridger, 1968), so that the form in the pan was probably the monohydrate. As the product cooled, the hexahydrate

was formed, taking all the free water in the process. This kind of drying increased the hardness of the granules. Some evaporation of water occurred too, since it was observed that granules stored in an air-tight bottle cured much slower than those curing in open air.

Drying. It was found that after curing, the granules could be dried easily to the monohydrate, while still retaining their strength. When drying was effected immediately after production, the granules became very weak and would never regain their strength. The observation indicated that some reaction continues even after the granules leave the pan as the free water spreads throughout inside the granules. The observation also indicated that on a commercial operation, the product could be dried, if needed, with the provision that a curing step be anticipated. An example of how the drying affected the strength of the granules is provided by the typical crushing strengths of MNP materials, is described below:

Crushing Strengths

Cured MNP	MNP Cured and Dried	MNP Dried Without Curing
4-6 lb	2-5 lb	0.4 - 1.5 lb.

Wetting. The granules which underwent the leaching experiment were soaked in water many repeated times and did not disintegrate. Residual granules from that experiment were still strong after the test. This was an important observation, since any slow-release fertilizer, although barely soluble, would greatly speed up the release of its nutrients if disintegrated into smaller particle sizes.

Storage. The MNP and MNPK products left in an open atmosphere did not absorb moisture, remaining dry and hard. This would be expected

since magnesium ammonium phosphate is very insoluble and non-hygroscopic. The dry feed subjected to a bag storage test, showed no bag set and no caked lumps after one and three months storage. The conditions of the test were equivalent to those in the bottom bag of a 20 50-pound bags stack (12).

A very sensitive test was developed to detect the loss of ammonia during storage. The test consisted of introducing a test tube, which had its tip wetted with HCl solution, inside a bottle containing the material where ammonia loss was to be detected. The bottle was then tightly closed. When ammonia was being released, typical crystals of NH_4Cl started to be formed and built up at the tip of the tube. It was found that granular products were very stable with respect to ammonia losses, and that the finely pulverized feed mix was as stable as the unmixed granular MAP, which normally contains some free ammonia. This indicated that the dry mix would not react in storage. It is recommended, however, that the raw materials sea water magnesia and MAP be stored separately, except for the batch to be immediately used. This recommendation would pre-empt accidents such as wetting the feed, which would inutilize it. It would also eliminate a source of dust in the plant.

Slow-Release Characteristics

The resistance to leaching of two experimental products, MNP and MNPK, was studied and compared with leaching rates of MAP and MAGAMP. As an additional effect, it was also intended to observe the relation between granular sizes of MNP and MNPK and rates of leaching. It was expected that the leachability of the controls, MAP (soluble) and MAGAMP (insoluble), would bracket the leachability of the MNP and MNPK products.

The test developed did not involve nitrification or other release mechanisms other than chemical leaching. This undoubtedly constitutes a limitation on the results, which nevertheless provide an important starting point for the evaluation of the slow-release characteristics of the product being manufactured.

Experimental

A rack was fabricated to support milk gallon jugs (see Figure 6), which constituted the leaching columns. Each column was packed with 3 (three) kg of washed and dried sand. The fertilizer material was mixed thoroughly with the top 2 (two) inches of sand. The amount of fertilizer in each column was the equivalent to 75 pounds of nitrogen per acre. Each column was thereafter leached 8 (eight) times with the equivalent of 1 (one) inch of water per leaching. Each time the columns held the leaching waters for two or three minutes before starting to drain. Each column was emptied of water first by gravity and then by a 1/3 atm suction to overcome the capillary action of the column. Thus, leachates of about 400 ml were collected each time from every column. Then each leachate was analysed with respect to N, P_2O_5, K_2O and Mg. Knowing the initial amounts of those nutrients in each column, a leaching pattern was calculated. The analytical methods used are described in detail in Appendix A. Table 7 lists the materials tested in the leaching experiment.

Results and Discussion

The final results are the cumulative percentages of nutrients leached from each column, per leaching, and are given in Table 19. The main observations can be summarized in graphical form and are presented

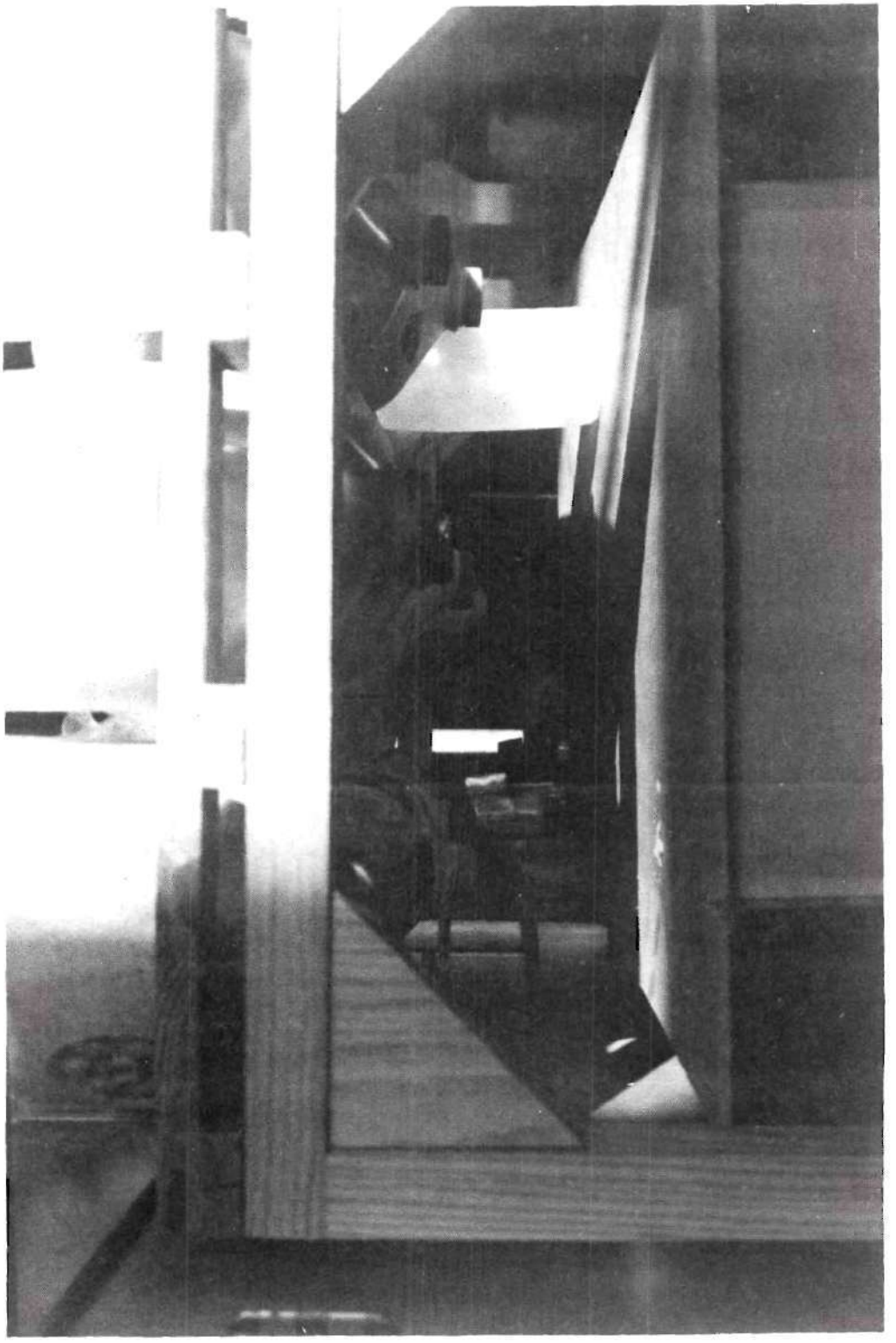

Figure 6. Leaching Columns.

Table 7. Key to the Leaching Columns, Granular Products

Column	Contents	Formula ($N-P_2O_5-K_2O-Mg$)
1	MNPK (-3/8" + 4 mesh)	7-32-5-7
2	MNP (-4 + 6 mesh)	8-32.5-0-10
3	MNPK (-6 + 8 mesh)	6-28-5-8
4	MNP (-8 + 12 mesh)	8-32.5-0-10
5	MNP (-12 + 32 mesh)	8-31-0-8
6	MNP (-32 mesh)	7-32.5-0-8
7	MAGAMP (-6 + 8 mesh)	6.5-27-6-8
8	MAP (-4 + 6 mesh)	13-52-0

in Figures 7-11.

From Figure 7 it is noted that the N from the MNP product was released slower than the N from MAP, but faster than the N from MAGAMP. Approximately 60% of the N from MAP was leached after 4 inches of water, while only 4% of the N from MAGAMP and 12% from a typical MNP sample.

From Figure 8 it is observed that the release of K from MNPK products was comparable to that from MAGAMP, both being quite fast. Thus approximately 70% of the initial total K was leached from the columns containing either MNPK or MAGAMP after 8 inches of water was applied.

The phosphorus was very resistant to leaching from any MNP or MNPK product (Figures 9 and 10). Magnesium was extremely resistant against leaching from either material. From Figures 9 and 10 it is also observed that the leaching of the nutrients was incongruent, and

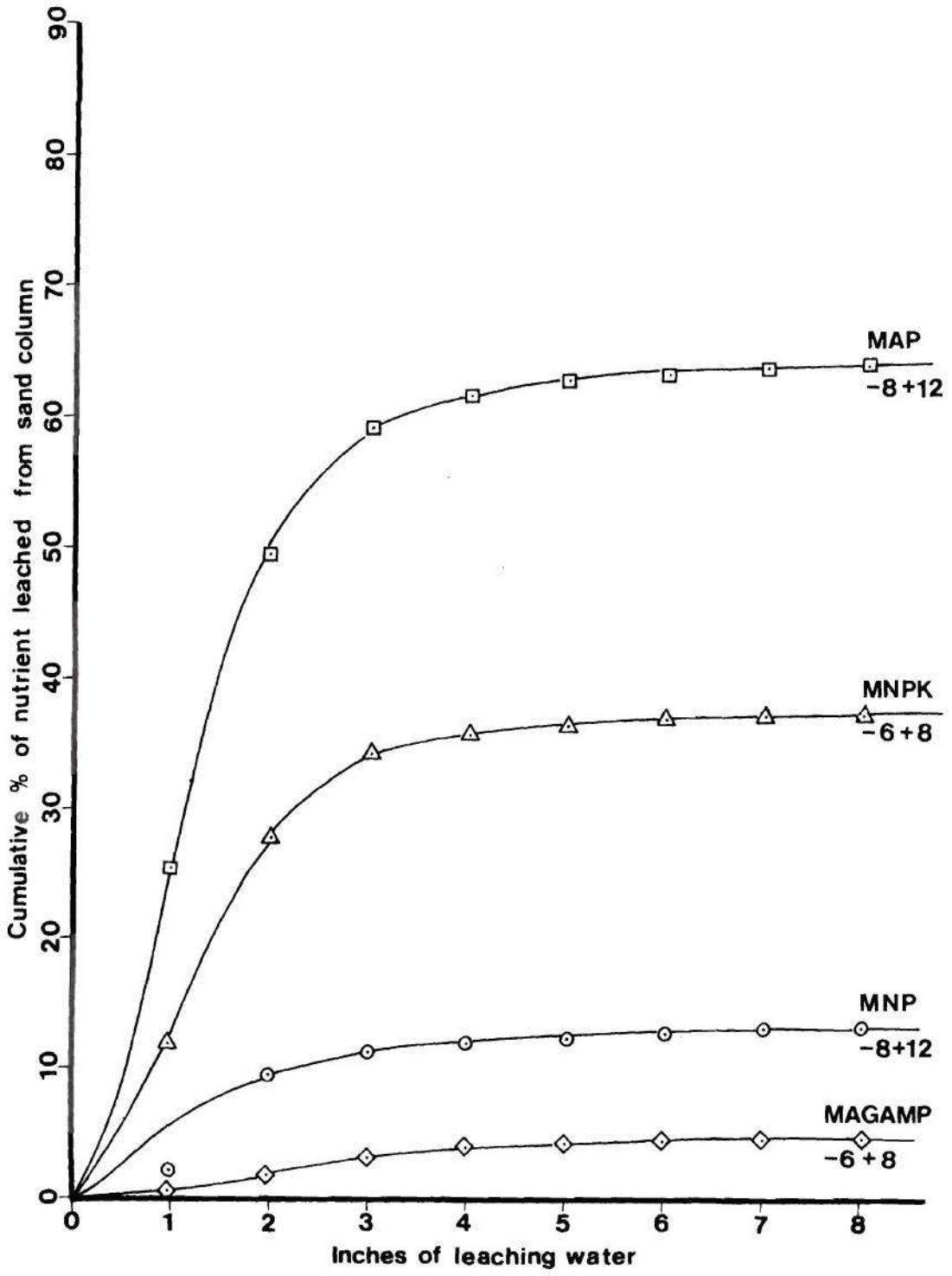

Figure 7. Relative Leachability of Nitrogen from Several Sources. Granules Size Indicated (Screen Mesh).

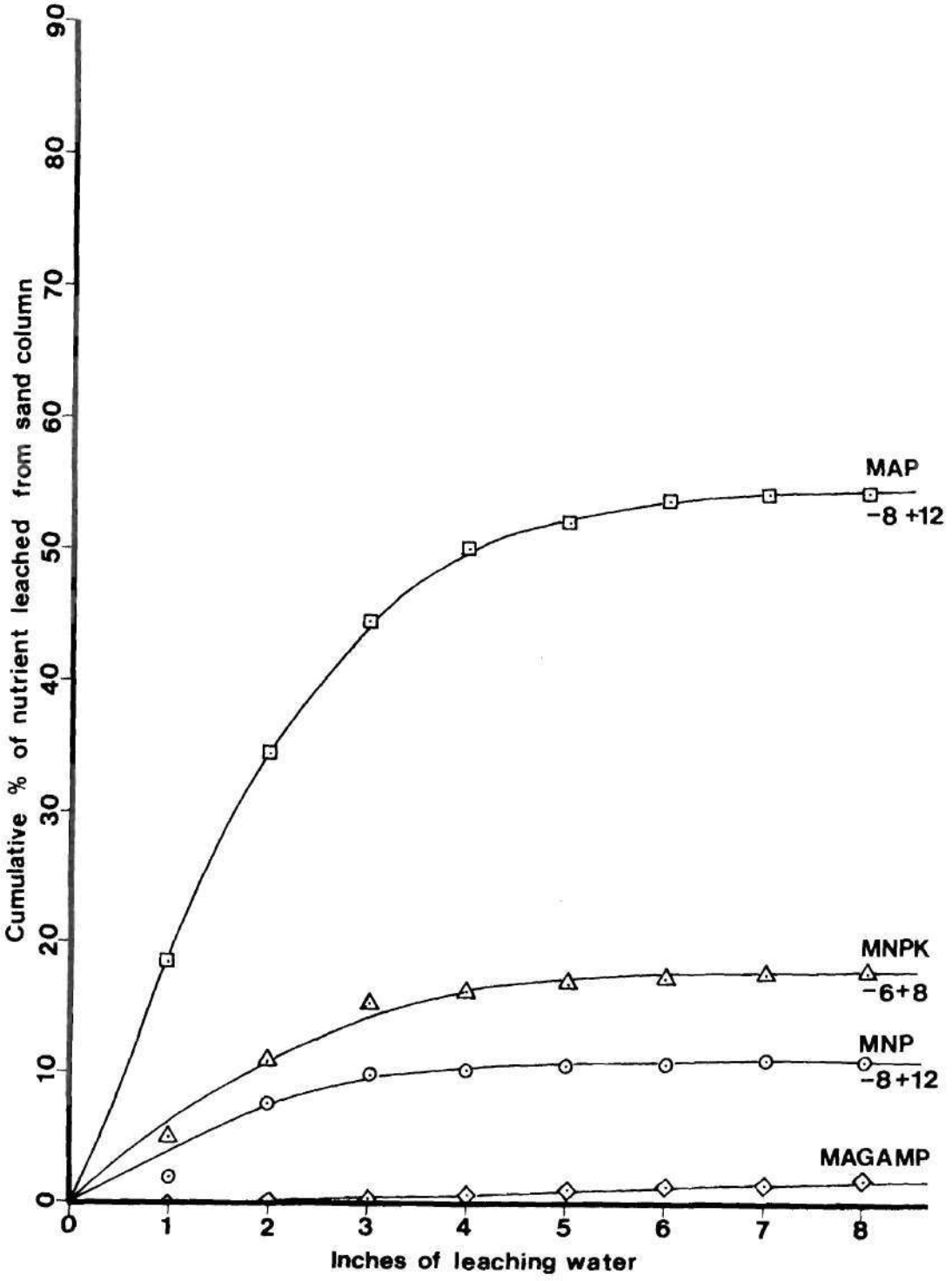

Figure 8. Relative Leachability of Phosphorus from Several Sources. Granules Size Indicated (Screen Mesh).

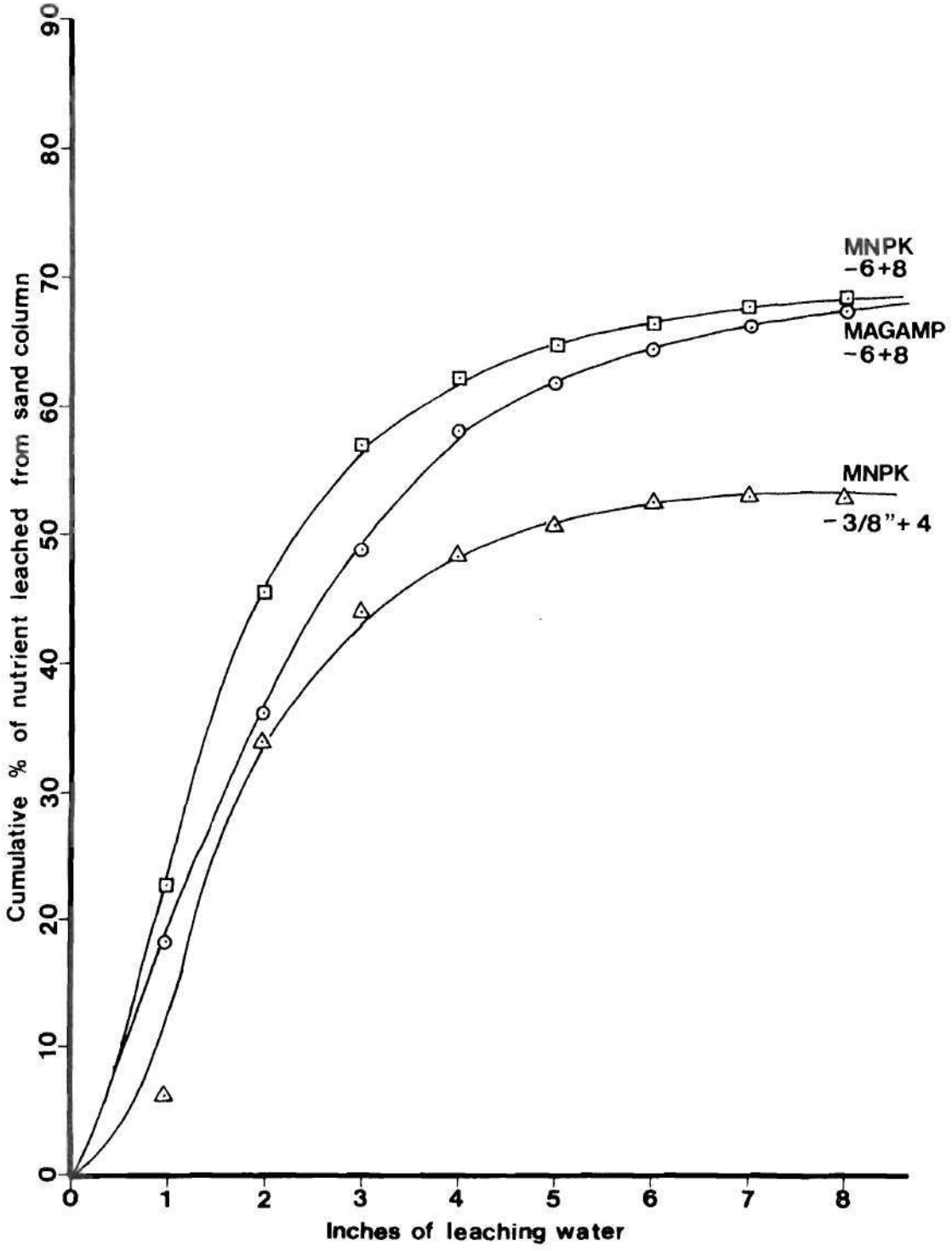

Figure 9. Relative Leachability of Potassium from Several Sources. Granules Size Indicated (Screen Mesh).

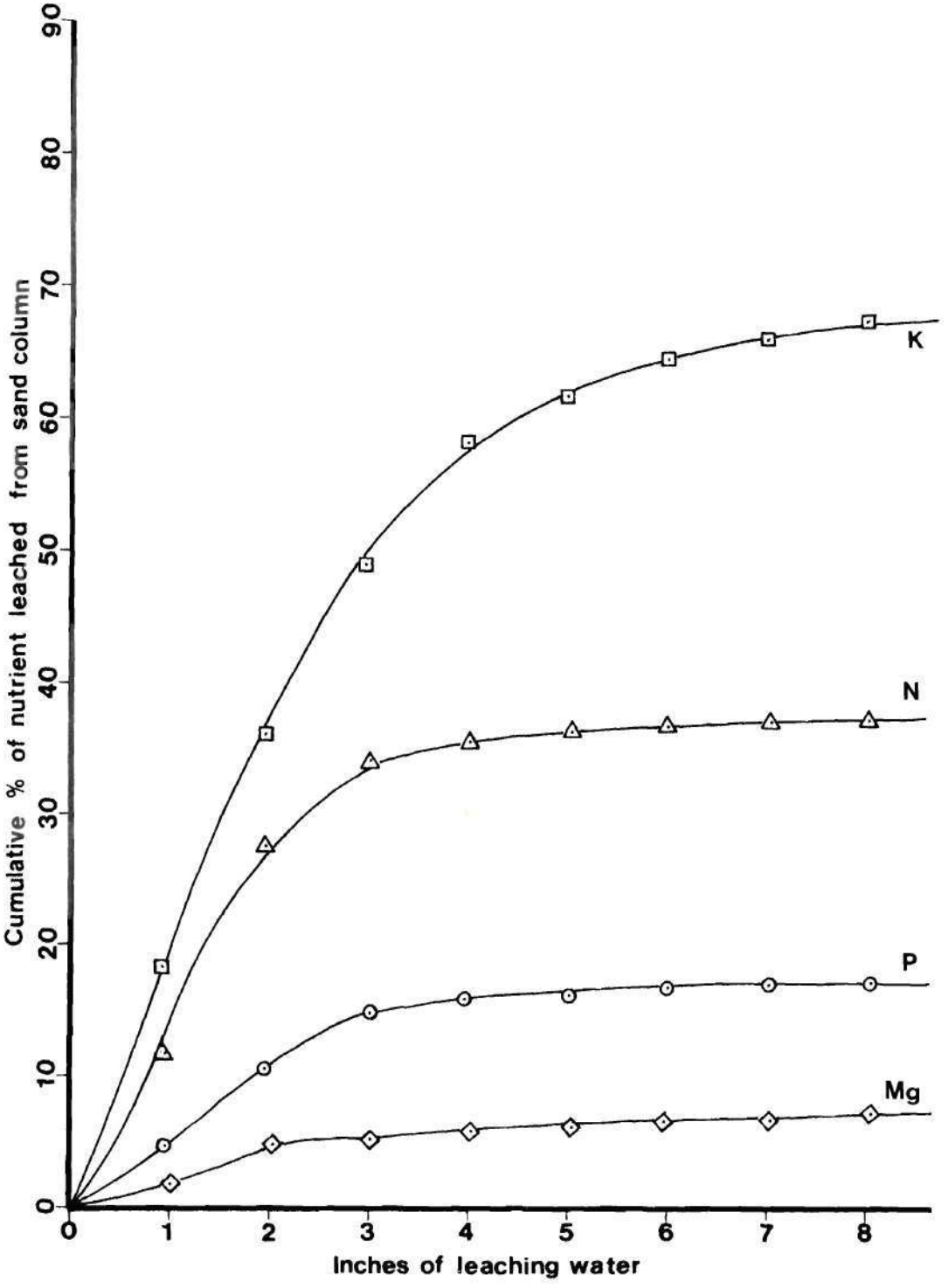

Figure 10. Incongruent Release of Nutrients from MNPK (-6+8 Mesh).

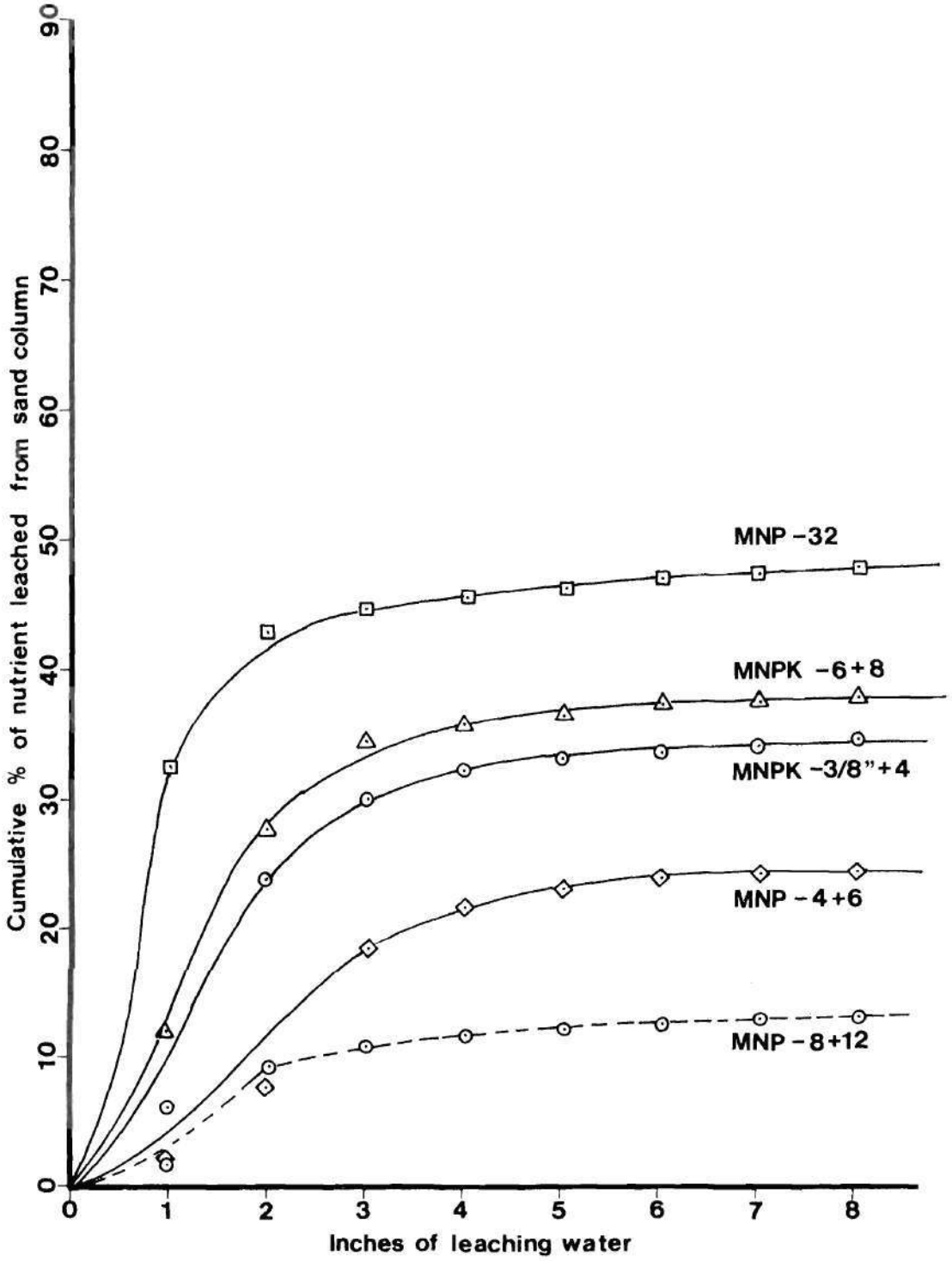

Figure 11. Effect of Granule Size on Nitrogen Release from MNP and MNPK. Granules Size Indicated (Screen Mesh).

K > N > P > Mg was the decreasing order of leachability.

Figures 9 and 11 indicate that the -32 mesh fraction of the MNP product was slightly better than MAP (-8 + 12 mesh) as a slow-release material, and about equivalent to the slurry products (Figure 13).

Figure 11 also shows that MNP granules released N more slowly than MNPK granules of the same size. *It is possible that* K salts interfered with the solubility of $MgNH_4PO_4$, resulting in the formation of insoluble K compounds. Another possibility is that K salts, being rapidly leached, leaves the granules very porous, and thus subject to faster leaching. In the same illustration it is noted that the rule of thumb for leaching (the rate of release increases monotonically as the granular size decreases) breaks down in this test. MNP (-8 + 12 mesh) and (-12 + 32 mesh) were slower in releasing N than larger granules. This phenomenon may occur if the products are not physically nor chemically uniform throughout the range of particle sizes.

X-Ray Diffraction Characterization

As part of the effort to characterize the products from the granulation process, X-ray diffraction techniques were found adequate to define the extent or completeness of the reactions in each process, as well as to provide insight into the mechanisms of ammonia loss, delayed potassium release, and other release mechanisms. The above four points can be discussed as follows.

A) Completeness of reaction. Consider the reactions:

$$MgO + NH_4H_2PO_4 \rightarrow MgNH_4PO_4 + H_2O \qquad \text{(III-3)}$$

$$MgO + (NH_4)_2HPO_4 \rightarrow MgNH_4PO_4 + NH_3 + H_2O \qquad \text{(III-4)}$$

Since fertilizer grade MAP (13-52-0) is a mixture of roughly 80% mono, 20% diammonium phosphate, both reactions (III-3) and (III-4) occur in the processes. However, it might be expected that in both processes the reactions are incomplete because of short residence times in the equipment. It is therefore necessary to define the extent of the reactions by quantitative determination of $MgNH_4PO_4 \cdot H_2O$, $MgNH_4PO_4 \cdot 6H_2O$ or of unreacted $NH_4H_2PO_4$, MgO, $Mg(OH)_2$ on a typical sample.

B) Losses of Ammonia. In the granulation process, a main concern is the possibility of substantial losses of ammonia. Such losses can be produced through reaction (III-1), but also possibly through undesirable reactions yielding magnesium phosphates, such as $Mg_3(PO_4)_2 \cdot nH_2O$, $MgHPO_4 \cdot nH_2O$, $Mg(H_2PO_4)_2$, etc. In any case, the presence of magnesium phosphates of any form indicates release of ammonia. Such release can be partially reabsorbed by the water in the slurry process but is likely to be entirely lost in the granulation process. One of the intentions of this work was to detect any magnesium phosphate in the samples.

C) Leaching Mechanisms. It was observed from the leaching experiments that nutrients were not released at the same rates from MNP and MNPK products. Examination of leaching residues would provide insight into leaching mechanisms, or would help to identify reactions occurring during leaching.

D) Delayed Release of Potassium. It was observed during the leaching experiments that there was a delay in the release of potassium. This delay was associated with a faster release of nitrogen from the MNPK products. Therefore, the possibility that the delay in the release of potassium was due not only to occlusion of KCl by insoluble salts,

but also due to formation of some $MgKPO_4 \cdot nH_2O$, had to be investigated. Presence of NH_4Cl would reinforce this hypothesis.

Experimental

The detailed technique for the X-ray examination of the pilot-plant materials is described in Appendix D. The following samples were selected for analysis.

Table 8. X-Ray Analysis Samples--Granular Materials.

Sample Identification	Source
G-1	MAGAMP from W. R. Grace & Co.
G-4	MNP product, (-4 + 6) mesh
G-6	MNPK product, (-6 + 8) mesh
G-7	MNP product, after leaching
G-8	MNPK product, after leaching
G-10	MNP product, dried for 3 hrs at 105°C

Sample G-4 was selected for the quantitative analysis of $MgNH_4PO_4 \cdot 6H_2O$. The X-ray quantitative technique is described in Appendix C.

Results and Discussion

The results obtained and given in Appendix D (Table 21) are summarized in Table 9.

Table 9 shows that with the exception of the dried product G-10, all samples contain the hexahydrate as the major constituent. This fact indicates that the reaction advanced to the limit of the availability of

Table 9. Summary of X-ray Diffraction Characterization of Several Granular Materials

Compound	Samples					
	G-1	G-4	G-6	G-7	G-8	G-10
$MgNH_4PO_4 \cdot 6H_2O$	**	**	**	**	**	
$MgNH_4PO_4 \cdot H_2O$	*					**
$MgKPO_4 \cdot 6H_2O$	**		*		*	
MgO	X	X	X	X	X	
$Mg(OH)_2$	X	X				
$NH_4H_2PO_4$	X	X	X			X
$(NH_4)_2HPO_4$		X	X			
KCl			**			
$Mg_3(PO_4)_2$						
$Mg_3(PO_4)_2 \cdot 4H_2O$						
$Mg_3(PO_4)_2 \cdot 8H_2O$						
$Mg\ HPO_4 \cdot 3H_2O$	(a)					
$Mg\ HPO_4 \cdot 7H_2O$		X				
$Mg(H_2PO_4)_2$		X				
$Mg_2P_2O_7$						
NH_4Cl			X			

** Major component in mixture.

* Considerable presence.

X Traces.

(a) Strong overlapping of peaks with those of other major prevent positive identification.

water in the granule. Therefore water of hydration can be used as a measure of extent of reaction between MgO and MAP within the granule. For example, the sample G-4 was found to contain 2.78% free moisture. Weight loss at 105°C was 23.09%. Assuming that weight loss minus free water corresponded to water lost in the transition hexahydrate to monohydrate, a simple calculation indicated 55% $MgNH_4PO_4 \cdot 6H_2O$ in the sample.

With respect to ammonia loss it was difficult to positively identify several magnesium phosphates due to strong overlapping of their peaks with peaks of major components. The high extent of conversion indicates, however, that the most important source for ammonia loss is reaction (III-4) as previously mentioned.

With respect to potassium insolubilization, in the leaching experiments it was found that $MgKPO_4 \cdot 6H_2O$ was present in small amounts in samples G-6 and G-8. This indicates that magnesium potassium phosphate was formed during processing and that the compound resisted leaching.

It was not possible to verify to what extent the reactions (III-3) and (III-1) continued while the granules underwent leaching. It was verified, however, that all traces of MAP and DAP disappeared in the leaching residues.

The quantitative determination of $MgNH_4PO_4 \cdot 6H_2O$ in sample G-4 indicated 55.97% of the hexahydrate in the MNP granules (See Appendix D). In Appendix E it is shown that such figures correspond to a conversion of about 49% of the MAP and sea water magnesia feed. It is clear that the extent of reaction (III-3) will depend mostly on the water used in granulation.

Conclusions and Recommendations

The Process

The granulation process would require careful control. While it is probably true that in a larger pan imbalances in the granulation would be easier to avoid and correct, it must be still assumed that making the granules in a larger pan would be another art altogether. While the production at Georgia Tech totalled about 1,000 pounds, that experience should be useful as a general guideline. The information generated should not be relied upon for direct scale-up, for instance. It must be a recommendation that the process be proven on a commercial pan granulator.

The process has the advantage of dispensing drying and cooling. Moreover, the choice of dry feeds has the substantial advantage over phosphoric acid and anhydrous ammonia feeds, because of the convenience in handling, storage and transportation.

The Product

The overall physical properties of MNP and MNPK were excellent. The products were free-flowing, hard, non-caking, non-smelling, and non-hygroscopic.

Laboratory experiments suggest that MNP and MNPK should be good slow-release materials. The results obtained, however, are not adequate for extrapolation to field conditions. In actual soil, soil reactivity and exchange capacity and mainly bacterial action can make the outcome much different.

X-ray powder diffraction patterns showed that magnesium ammonium phosphate was the main component of the granular complex fertilizer

produced. The extent of the reaction

$$MgO + NH_4H_2PO_4 \rightarrow MgNH_4PO_4 + H_2O \qquad \text{(III-3)}$$

in the granulation depended on the amount of water used in the process. During the curing process the free water present in the granule eventually became water of reaction and crystallization. This hypothesis was confirmed by free moisture analyses, drying experiments and by the X-ray diffraction patterns obtained for several granular products and for the dried granules.

It was verified that the ammonia losses observed in the granular process are mostly due to completion of the reaction (III-1). This was in agreement with the ammonia loss versus moisture data previously reported (Table 4). The identification of several magnesium phosphates was not possible because of strong overlapping of their characteristic peaks with peaks of major constituents; however, their presence could not be discarded.

There are indications that at least some reaction took place during wetting and leaching in the column. For example, while the quantitative analysis of $MgNH_4PO_4 \cdot 6H_2O$ in MNP indicated 55% of that compound in the fertilizer granule, which corresponded to about 49% conversion of the reactants in the dry feed, the leached nitrogen was much less than the unconverted nitrogen in MNP. Reinforcing that observation, residues from leaching showed almost pure $MgNH_4PO_4 \cdot 6H_2O$.

A great improvement for the MNP and MNPK process would be the use of MAP with lower diammonium phosphate content. This would reduce the soluble N and almost certainly eliminate ammonia losses in the process,

which are very significant. Powder MAP (See the Glossary) would have the advantages of a favorable $N:P_2O_5$ ratio and of dispensing grinding.

The main disadvantages of the product are the low N/P_2O_5 ratio and also the probable excess Mg that it carries. While this Mg cannot get a premium price for the fertilizer, it still brings with it the danger of building up the soil pH after repeated applications.

The excellent physical properties of the material tempt the author to recommend its use for coating urea or other soluble nitrogen compound. A high nitrogen analysis fertilizer with possible slow-release characteristics might result.

Suggested Agronomical Uses

Because of the slow-release characteristics, the products MNP and MNPK may be recommended for plants with a long growing season, such as trees and ornamentals. The readily soluble part may be an advantage over totally insoluble fertilizer, since it would provide nutrients necessary for early growth and establishment.

CHAPTER IV

SLURRY METHOD FOR THE PRODUCTION AND USE OF MAGNESIUM AMMONIUM PHOSPHATE BASED FERTILIZERS

Introduction

A process for the production of a slurry fertilizer in which the base component was magnesium ammonium phosphate was developed. A very fine precipitate was formed when sea water magnesia and MAP were reacted inside the tank of hydroseeding equipment. Agitation was provided by rotating blades and, in some equipments, by pumping and recirculation of the slurry. The main reaction was, as before:

$$MgO + NH_4H_2PO_4 + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \qquad (IV-1)$$

Incorporation of KCl and micronutrients could possibly provide an inexpensive way of obtaining and applying slow-release potassium and micronutrients.

The slurry was named HYDROMIX, and typical dry mix (unreacted components) analyses were 7-35-7-11 ($N-P_2O_5-K_2O$-Mg) and 6-28-18-9. The grades can vary because of the different grades of MAP in the market. When DAP was used, the dry mix grade was 12-30-12-9. The slurry could be easily handled when the solids content was 10-20%, which corresponded to a settled volume of 20-40% of the total volume of the slurry and a density of .85-1.7 pounds per gallon.

Hydromulchers combine seeding, mulching and fertilization in one

single operation. Fertilizers can be used in any form and mixed to any proportion. Hydromulchers, also called hydroseeders or hydrograssers, are produced in a wide range of sizes from 150 gallons to 3000 gallons of nominal tank capacity. Around 27 different (13) models from six manufacturers are commercially available in the U.S. in that range. The acreage range covered by such equipment per application is up to 5 (five) acres, in a normal application. While presently limited to grassing, such equipment could be converted easily to crop fertilization. This type of equipment would be ideal for the application of powdered fertilizers, such as, for example, phosphate rock.

Production and Use

Raw Materials

The raw materials used in the production of HYDROMIX were exactly the same described in the production of MNP and MNPK.

Feed Preparation

In the laboratory both granular and pulverized MAP reacted with MgO to yield the same level of insoluble nitrogen. Therefore, in the manufacture of HYDROMIX slurry granular MAP was used. Pulverized MAP went faster into solution (see Table 11) and this would constitute an important element in a field application. However, powder MAP is not widely available as is granular MAP.

The raw materials did not have to be premixed. It was found that order of addition was immaterial with respect to conversion to insoluble nitrogen and phosphorus. For corrosion prevention, it would be desirable to add the basic component first. However, in a practical situation, it

would be convenient to have premixed, bagged formulations. It must be noted th at the mixture was very dusty and that if premixing was a requirement, use of some air-tight equipment would be recommended. Table 10 exemplifies some of the formulations used throughout the testing efforts.

Table 10. Formulation of Experimental HYDROMIX (Dry Ingredients)

Material	Pounds of Ingredients Per Ton of HYDROMIX		
MAP (11-52-0)	1352	1111	-
Magnesia (57% Mg)	408	334	330
KCl (0-0-62)	241	555	383
DAP (18-46-0)	-	-	1290
Final Formula (N-P_2O_5-K_2O-Mg)	7-35-7-11	6-28-18-9	12-30-12-9

Laboratory Production

Some laboratory work was performed before the method was tested in the hydroseeding equipment. In the laboratory, test slurry was made in 500 ml bottles, by filling them with 250-300 ml of distilled water together with about 12 grams of sea water magnesia and ammonium phosphate mixed to yield magnesium ammonium phosphate. A magnetic stirring bar was put inside the bottle; then the bottle was capped tightly and put on a magnetic stirrer plate. The agitation achieved was less vigorous than that obtained inside the tank of a commercial hydroseeder. Only

slight heating-up effects were observed. The observations are summarized in Table 11 below, and a discussion follows.

Table 11. Summary of Laboratory Production Data for HYDROMIX Slurries with Different Ammonium Phosphate Feeds

Ammonium Phosphate	Minimum Mixing Time (Minutes)	pH	% Insoluble Dry Basis	% N Insoluble	% P Insoluble
13-52-0	30	7-7.3	69-75	64-70	72-75
18-46-0	25	9-9.5	62-66	53-56	79-81
13-52-0 Powder	15	7-7.2	65-75	63-70	72-75
11-52-0	30	6.4-6.9	66-69	63-70	68-72
11-52-0 Powder	15	6.4-6.9	66-69	63-68	68-70

Observations: MgO feed was Magox 98 HR. This is an insoluble base, forming insoluble hydrates. MAP and DAP used contained around 12% water insoluble mass, and about 8-10% water insoluble N and P_2O_5.

Reaction Time. It was found that granular fertilizer grade ammonium phosphates do not easily go into solution. 18-46-0 was brought faster into solution than the granular MAPs. Crystalline feedgrade mono ammonium phosphate (98% mono, 2% diammonium phosphate) dissolved faster but an actual method could never be based on such feed because of its cost. Powder MAP also dissolved fast; unfortunately for the grassing experiments such material was not available. The times reported in Table 11 must be regarded on a relative basis. Actually the agitation pattern and intensity would vary from one hydromulcher to another.

Ammonia Loss. When DAP reacted with MgO the pH was so high in the slurry that ammonia release was evident. Actually the equilibrium $NH_3 + H^+ \rightleftarrows NH_4^+$ can be shown to depend on the concentration of hydrogen ion, i.e., on the pH. This is described visually in Figure 16, in Appendix A. It is clear that solutions with pH above 8 would not be desirable. Ammonia losses would be particularly high when the slurry is being sprayed. All sources of MAP gave slurries with a satisfactory pH.

Insolubilizaton. It may be observed from Table 11 that an average 70% of the reactants were found to be insoluble when MgO reacted with MAP and a slightly lower percentage when MgO reacted with DAP. In that table, conversion to magnesium ammonium phosphate was calculated from the percentage of insoluble phosphorus. It must be noted, however, that commercial fertilizer grade ammonium phosphates contain about 10% (of the total) of water insoluble phosphorus and nitrogen, usually as metal ammonium phosphates originated from impurities in the acid. The results obtained for the reaction with DAP differed somewhat from those presented by Bridger and McCullough (1963). The difference can be explained by a different way of calculating conversion and also because the DAP used in that work, 16-48-0, is somewhat different from the now established grade for DAP. The important conclusion from the observations made was that the ionic strength of the slurry made by this process would be substantially slower than that when a soluble fertilizer is used, making it a safer fertilizer to apply.

Introduction of Potassium Chloride. Bridger and McCullough (1963) had observed that KCl did not interfere with the MgO-DAP reaction. Because of the excess ammonium, potassium ions did not affect the conversion

to magnesium ammonium phosphate. However, in the present study, it was clear that KCl interfered with the MgO-MAP reaction. It was observed that $MgKPO_3 \cdot 6H_2O$ was formed in a substantial way. From the leaching experiments, it was also found that the release of potassium was delayed from the HYDROMIX slurry. The observation that potassium substituted the ammonium in the magnesium ammonium phosphate crystal was consistent with the observations by Ando et al. (1967) in which it was noticed that potassium salts promoted the decomposition of magnesium ammonium phosphates during the drying of fertilizers, yielding in the process insoluble potassium compounds.

Field Production and Use

The formulations presented in Table 10 were used in many field applications. The application rates per plot ranged from a low of 50-200-75-100 ($N-P_2O_5-K_2O$-Mg) pounds per acre to a high of 450-1800-675-1300 pounds per acre. Slightly different planting procedures and details such as site soil preparation and micronutrient rates make it proper to describe each test or group of tests individually. This is so done in Chapter V. Here a general mixing procedure is described, and some observations on the production of HYDROMIX on the fields are given.

At the site to be planted, the hydromulcher tank was filled with water. Then agitation started and the dry mix fed to the tank. In about five minutes the MAP granules start to get soft and to disintegrate, eventually going into solution and reacting with the magnesia to form magnesium ammonium phosphate. In the meantime, wood fiber cellulose was being fed to the tank. An organic binder known by the trade name of Curosol was also added. Finally, the seeds were added to the tank, and

the slurry was ready to be applied. The residence time of the slurry inside the tank depended on the distance between the site to be planted and the base of operation, which was usually near the water source. It was estimated that the residence time was about 30 minutes. In other instances, it was much less, and some undissolved, unreacted granules could be spotted. (The granules were coated with what seemed to be magnesium ammonium phosphate.) It was concluded that as long as a granular feed was used such problems would occur. Therefore, powdered MAP would be a better raw material for this process. A final observation would be that a strong ammonia odor was formed when slurries were made from DAP. The ammonia losses could not be measured, but they were believed to be serious, particularly since the slurry was sprayed to the air. In Figure 12 the method is described by photographs. It can be observed: the strong, vigorous agitation inside the hydroseeding equipment, and the application in an experimental plot with a small capacity equipment. A large capacity applicator is also shown in action.

Slow-release Characteristics

In a similar experiment as done with the granular products, the formulations described in Table 12 were tested with respect to resistance against leaching. The same observations made in Chapter III concerning the limitations of the tests apply in this case. It must be re-emphasized, however, that the test does provide a starting point for determining the rates of release.

Results and Discussion

The results in the form of cumulative percentages of each nutrient leached away from the column after each leaching are given in Appendix B.

The Feeding of Raw Materials to the Tank of the Hydromulcher.

The Agitation of the Slurry

The Planting of an Experimental Plot.

A Commercial Hydromulcher (1,500 gallons) in Operation.

Figure 12. Field Production and Use of HYDROMIX.

Table 12. Key to Leaching Columns Slurry Products.

Column	Contents	Formula (Dry Basis) ($N-P_2O_5-K_2O-Mg$)
A1	HYDROMIX (with MAP)	9-34-9-11
A2	HYDROMIX (with MAP)	9-34-9-11
B1	HYDROMIX 9 (with DAP)	12-30-12-9
B2	HYDROMIX 9 (with DAP)	12-30-12-9
C1	HYDROMIX (with powder MAP)	9-34-9-11
C2	HYDROMIX (with powder MAP)	9-34-9-11
D1	Dry-Mix (with MAP)	9-34-9-11
E1	Dry-Mix (with DAP)	12-30-12-9

Such results were condensed in graphical form and the main observations may be inferred from Figures 13-15.

It is observed that roughly 40 to 50% of the N in the slurry was slowly soluble. About 30% of the N was in solution at the time the slurry was ready to be applied. Figure 13 also shows that the N released from the HYDROMIX prepared with DAP was rather low. Possibly some ammonia was lost during the manufacture and leaching of the slurry, which would not be surprising due to the high pH. It must be recognized, however, that a higher conversion to $MgNH_4PO_4$ is obtained with the DAP reaction, also due to the excess NH_3. Figures 13 and 14 show that P and Mg are much more resistant to leaching than nitrogen. This observation can be explained for MNPK products if it is assumed that insoluble magnesium phosphates are formed in the granules or down the leaching columns,

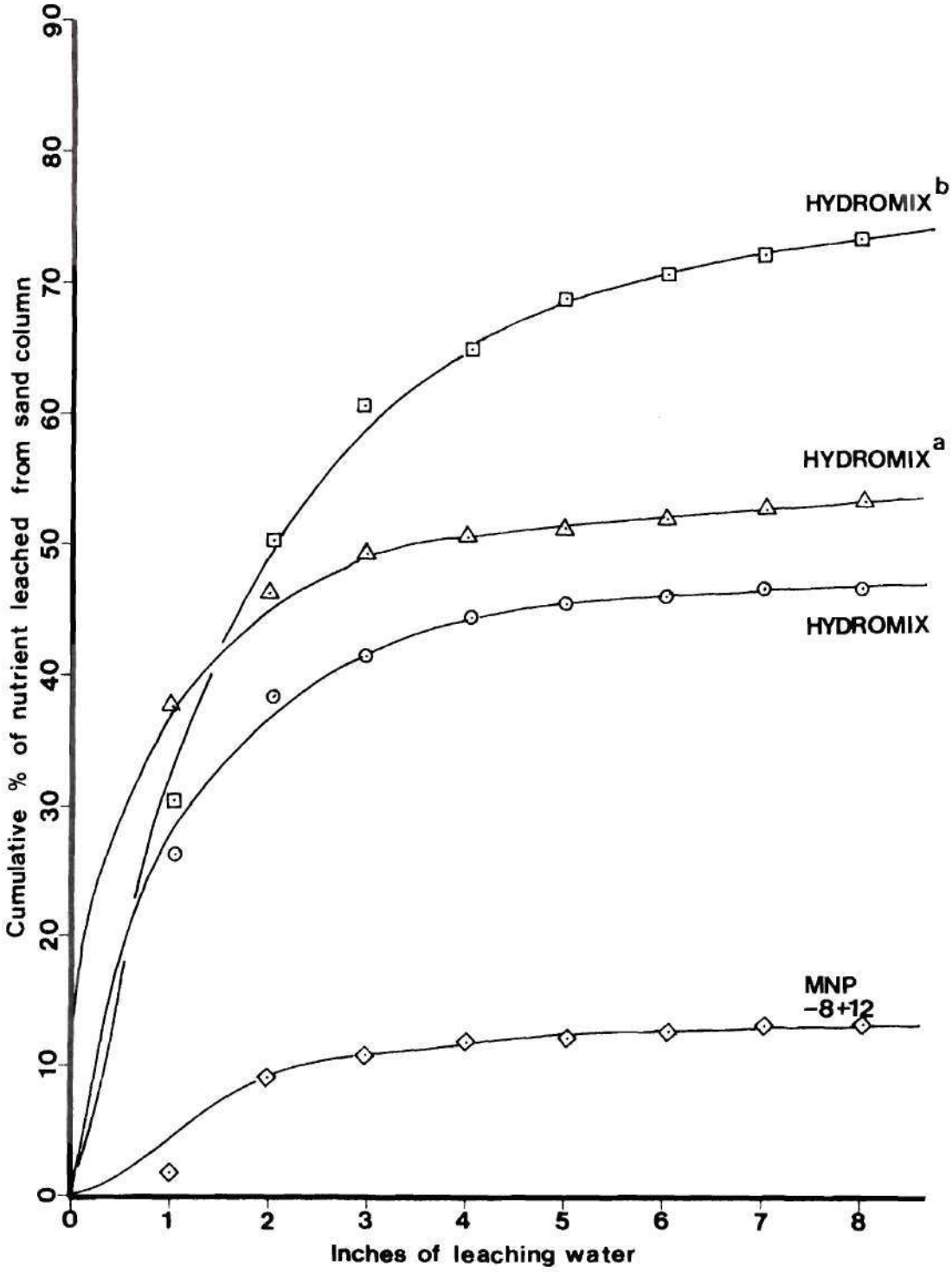

Figure 13. Nitrogen Leachability from HYDROMIX as Compared with Granular MAP and MNP. Superscript "a" Indicates HYDROMIX Prepared with DAP. Superscript "b" Indicates Unreacted, Unslurrified HYDROMIX.

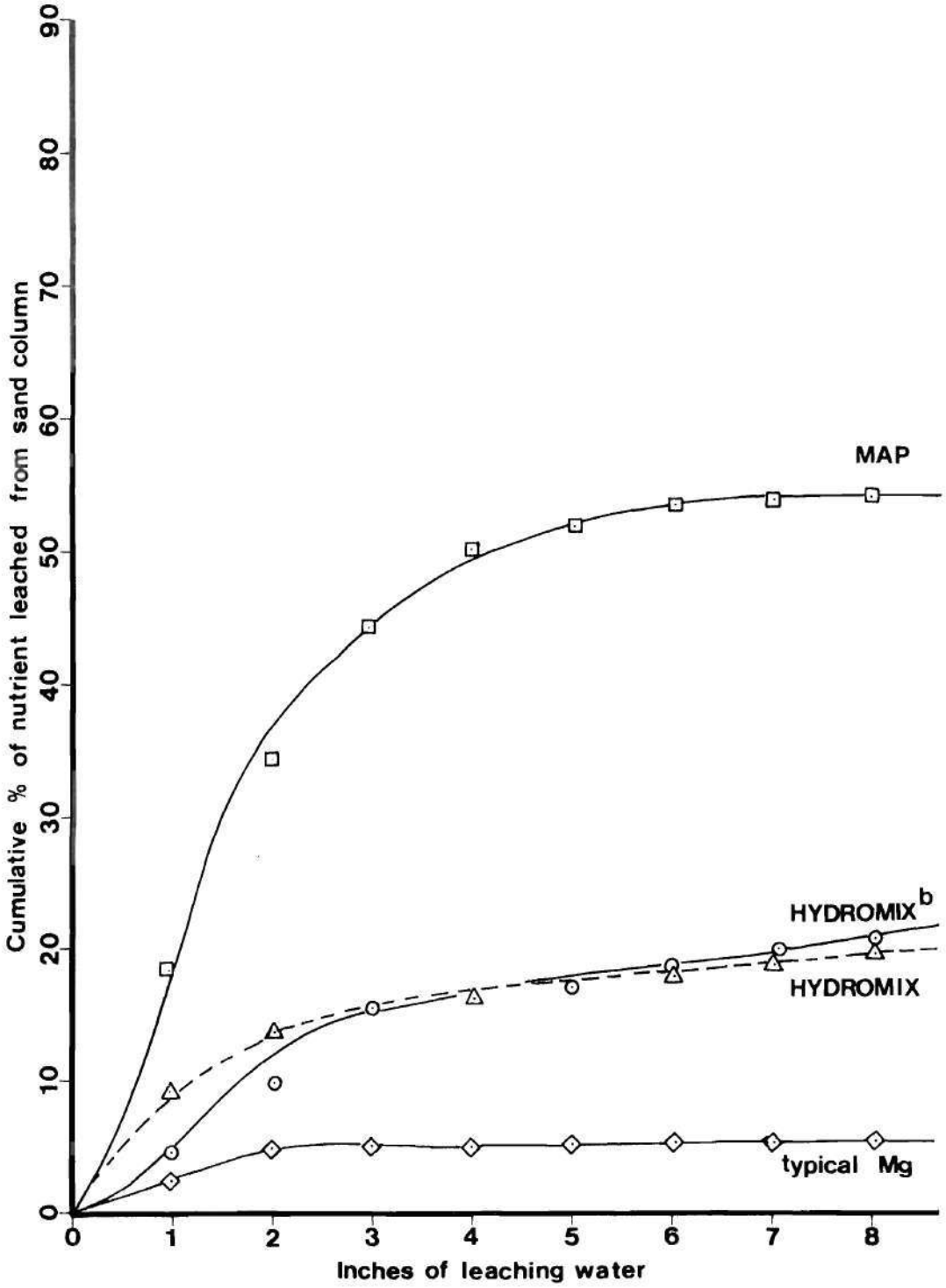

Figure 14. Phosphorus Leachability from MAP, HYDROMIX and Typical Magnesium Leachability from HYDROMIX. Superscript "b" Indicates Unreacted, Unslurrified HYDROMIX.

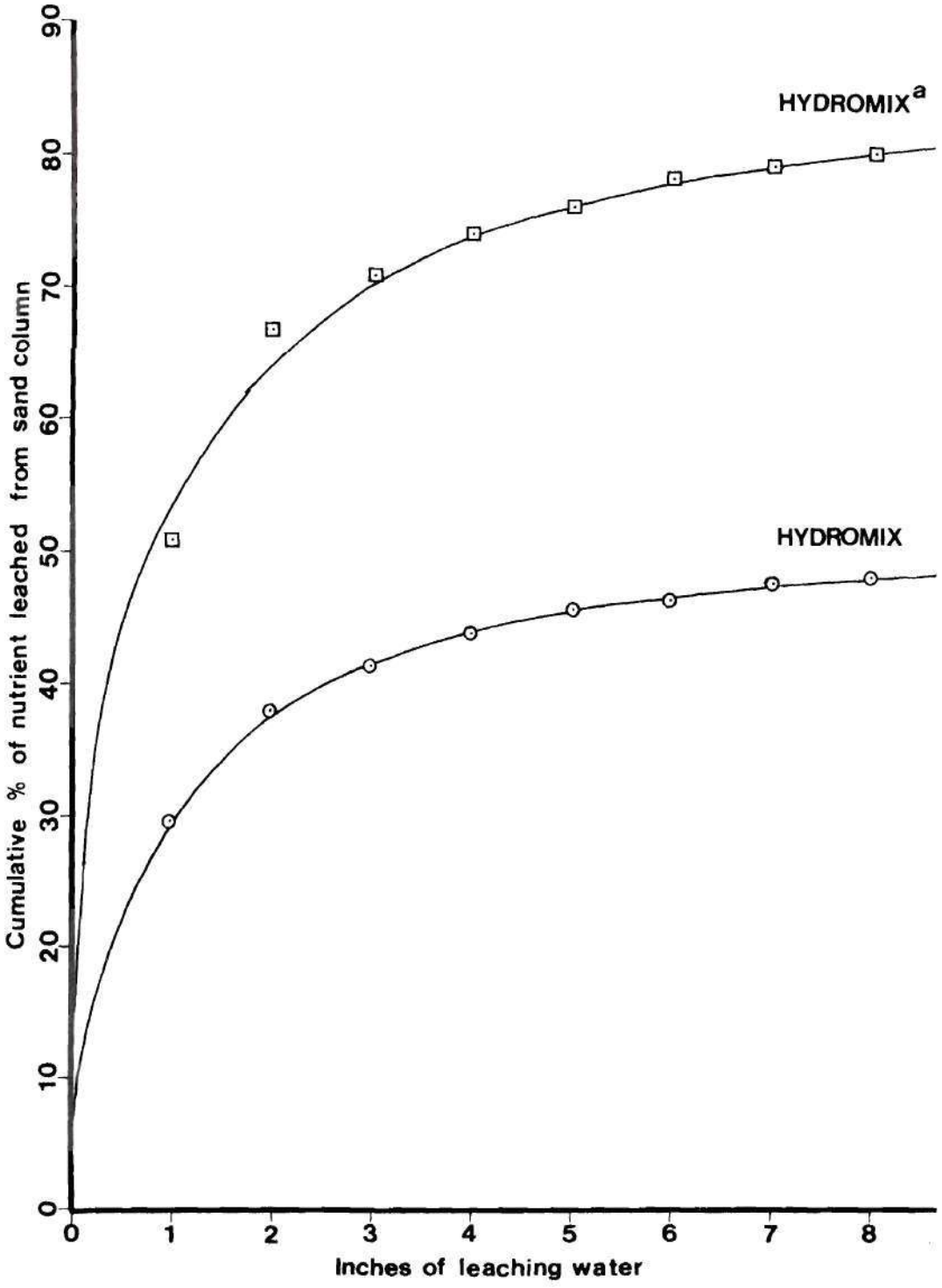

Figure 15. Potassium Leachability from HYDROMIX. Superscript "a" Indicates HYDROMIX Prepared with DAP.

which would be consistent with the thermodynamics of the system.

Figure 15 indicates that the K from the HYDROMIX is somewhat resistant to leaching. It is noted here that X-ray powder diffraction analyses have shown that $MgKPO_4 \cdot 6H_2O$ is the most prominent K compound in the slurry cake.

It is also observed that the HYDROMIX method is better than granular MAP with respect to resistance against leaching.

X-ray Characterization

In order to characterize the HYDROMIX slurry, insolubilization of nitrogen and phosphorus were not sufficient. The delay in the release of potassium was too great in order to be explained by occlusion of KCl by the $MgNH_4PO_4 \cdot 6H_2O$ precipitate alone. Qualitative X-ray examination elucidated the problem, identifying $MgKPO_4 \cdot 6H_2O$ as the main potassium compound in the slurry cake.

Unfortunately, leaching residues for the slurry could not, for practical reasons, be collected for X-ray examination. A solubilization residue was, however, collected and its examination rendered approximate information about the leaching mechanisms.

Experimental

The procedure for the X-ray powder diffraction study is presented in Appendix C. The materials listed in Table 13 were examined.

Table 13. Key to X-ray Analyses. HYDROMIX Slurries

Sample	Description
S.1	Slurry cake, filtered, washed, dried in air.
S.2	Slurry cake, residue from 12 (twelve) successive slurrifications and filtrations; dried in air.

Results and Discussion

The powder diffraction patterns obtained were calculated and listed in Table 21, in Appendix C. The observations are summarized in Table 14 below.

Table 14. Summary of X-Ray Diffraction Characterization of HYDROMIX Slurry Cakes

Compound	Samples	
	S-1	S-4
$MgNH_4PO_4 \cdot 6H_2O$	**	**
$MgNH_4PO_4 \cdot H_2O$		
$MgKPO_4 \cdot 6H_2O$	**	**
MgO		
$Mg(OH)_2$		
$NE_4H_2PO_4$		
$(NH_4)_2HPO_4$		
KCl	X	X

**Major component in Mixture

XTraces

It was clear that $MgKPO_4 \cdot 6H_2O$ was the main potassium component of the slurry cake. That compound is a slow-release K and P fertilizer. It is, however, much more soluble than magnesium ammonium phosphate, particularly under acid conditions (Salutsky and Steiger, 1964). The observation also indicates that Mn, Zn, Cu, and Fe ammonium phosphates could be formed. Those would be in a too small amount to be identified

by the procedure used.

A second valid observation was that the slurry cake was practically only magnesium ammonium and magnesium potassium phosphates. Therefore the procedure used for accounting the completion of the slurry reaction based on the insolubilization of phosphate was probably more adequate than the criterion of nitrogen insolubilization.

Conclusions and Recommendations

The Process

The real advantage of the process lies in its conception: production of an inexpensive slow-release fertilizer, from non-premium intermediates and with almost no processing.

The slurry method, by itself, has all the advantages of fluid application. It can be said that while granulation of MNP and MNPK was an art, the slurry method is so simple that no art was involved in the use of HYDROMIX.

Powdered MAP should be a better raw material, and future testing should include that material.

The laboratory testing was not expected to simulate actual field mixing and reaction. In the future, actual measurements on site should be made or a small scale applicator be built and the agitation studied.

The Product

The fertilizer formed was a surprisingly good slow-release material, in spite of the fact that it was so finely divided in the slurry. The possibility of obtaining a low-cost potassium slow-release fertilizer would be worth further investigation.

Formation of insoluble metal ammonium phosphates is known to occur when Mn, Zn, Cu, and Fe oxides react with ammonium phosphate solutions (Bridger, 1968). It should be expected that a slow release micronutrient be produced, at the expense of a slightly higher level of soluble nitrogen in the slurry. The actual verification of these reactions in the process here described would be a matter of future investigation.

Suggested Agronomical Uses

Grassing was thought to be the logical application of HYDROMIX. The slurry method combines seeding, mulching and fertilization in one single operation. Liming could very easily be included in the application. Very little or no soil preparation is needed for this planting method.

Actually many farm applications may be found. Foliar fertilization of soybeans, for example, should be highly interesting due to the favorable N:P_2O_5 ratio.

Other non-farm applications would include land reclaiming and sand dune estabilization, in which advantage would be taken of the slurry spraying to reach hard-to-get areas.

Finally, it may be suggested that, in the lack of hydrograssing equipment, the finely pulverized dry-mix could be mixed with wet soil in a concrete mixer, for example, or even with a spade or a hoe in a wood box; the dry powder should coat the soil particles while reacting due to the moisture and then the mixture could be broadcasted.

CHAPTER V

PRELIMINARY AGRONOMICAL EVALUATIONS

The agronomical evaluation of the products was not complete at the time of writing. Most testing still remains to be done. However, some conclusions from the field tests performed could be made and therefore should be presented.

Evaluation of MNPK Granules

The release of plant nutrients from MNP and MNPK as observed during the leaching experiments suggest that those materials would constitute safe, non-burning, slow-release fertilizers. While a number of applications would adequately test those properties, three usages were initially selected: shrub or tree planting, nursery sea oats seedling production, and sea oats seedlings transplantations to sand dune fields. The programs developed, if successful, would be immediately applicable to current State of Georgia fertilizer usage. Some results are available this far on the tree plantings only.

Tree or shrub planting is a major highway planting operation, together with grassing. While keeping in production otherwise idle land, trees have a role in preventing erosion, in controlling highway noise and glare and in the landscaping in general. It is obvious that a fertilizer offering long-term nutrient availability, as well as a lower mortality rate, would increase the efficiency of the planting and at the same time reduce the maintenance requirements.

Tree Planting No. 1

On a Georgia highway an experiment was made with several species of interest for roadside planting. Treatments consisted of the standard Georgia practice as control and of MNPK in substitution of the fertilizer used in the controls. The standard practice in Georgia (14) consists of mixing in the planting hole one-half cup of 5-10-15, 4-12-12 or 6-12-12, whichever is available, per foot of plant height, plus 1 (one) shovel of peat moss, 1 (one) cup of lime and 1/3 cubic foot of top soil. Sometimes the top soil and the lime are not used. The trees transplanted averaged three feet. In this case the fertilization rate used on the controls was 3/4 pounds of 5-10-15 per tree. The MNPK (6-17-6-8) application rate was 1/2 pound per tree. The MNPK granule size distribution was more spreaded than conventional (-6+16 mesh) fertilizer, being as follows:

Mesh	Percent
+4	20.0
-4+12	22.9
-12+32	34.1
-32	23.0

The plants were rated visually six months after planting. The results are shown in Table 15.

It can be suggested that a lower rate of application of MNPK was better than a higher rate of fertilization using 5-10-15. Long-term effects are still to be observed and many more plantings with other rates of fertilization ought to be made before a more conclusive statement.

Evaluation of HYDROMIX

The production and use of HYDROMIX was conceptually tied in to the fertilizer-seed-mulch formulation used on highway and commercial or other

Table 15. Six-Months Evaluation of Tree Planting

Experiment No. 1

Location: Stone Mountain, Georgia Planted: March 18, 1976

Observed: September 11, 1976

Experimentation: 1/2 lb. MNPK (6-27-6) Per Tree

Control: 3/4 lb. 5-10-15 Per Tree

Visual Rating Points: 0 - Dead 3 - Fair

1 - Very Poor 4 - Good

2 - Poor 5 - Excellent

Species		Ratings: Number of Trees According to Above Rated Scale 0	1	2	3	4	5	Total Trees Rated	Total Points
Virginia Pine	Controls:	7	3	6	5	3	3	27	57
	Experimentals:	6	1	2	6	7	6	28	81
Redbud	Controls:		1	1	1	2		5	8
	Experimentals:	1			1	1	2	5	17
Flowering Dogwood	Controls:		1	1	3			5	12
	Experimentals:			3	2			5	12
Fringe Tree	Controls:	2	4	4	2			12	18
	Experimentals:		2	2	3	3		10	27

grassing operations. Several grassing experiments were conducted along right-of-ways of Georgia roads. Treatments included controls in which the fertilizer was usually based on ammonium nitrate, ammonium sulfate, superphosphate and potash and experimentals in which the HYDROMIX was produced from sea water magnesia, MAP or DAP and KCl. Three test sites were planted in which rates of application and other conditions such as site preparation and mulch used varied considerably.

Grassing Experiment No. 1

The planting was done in late October, 1975. The site was a roadside bank along I-400 in Cummings, Georgia. The soil was landfill, rocky and poor in nutrients, especially nitrogen. Table 16 details each fertilizer-seed-mulch formulation used. Please note that formulations 1, 3, 5, 7, 9 and 11 generate HYDROMIX slurries.

The following observations have been recorded.

The early establishment and growth in all plots were slow. Neighboring plantings in which the seed bed was prepared by rolling the ground after seeding and in which hay and asphalt emulsion were used as mulch did much better in that respect.

In six-months eventually all plots were covered except for blanks in which no fertilizer and mulch or no fertilizer had been applied. Those plots were completely bare. The growth was, however, too slow so that signs of erosion were visible. The 5-6-7 group did better overall than both the 1-2-3 group and the 9-10-11 group. In this last group the grass growth, color and appearance was vigorous and good, but little clover survived the high rates of fertilization.

In one year, the whole area was covered including the blanks

Table 16. Grassing Experiment I. Formulations.

	Experimental Plot #1	Control Plot #2	Experimental Plot #3	Seed Only Plot #4	Experimental Plot #5	Control Plot #6	Experimental Plot #7	Seed & Mulch Only Plot #8	Experimental Plot #9	Control Plot #10	Experimental Plot #11
N Rate, lb/acre	75	75	75	--	145	145	145	--	450	450	450
P_2O_5 Rate, lb/acre	300	150	192	--	580	150	371	--	1800	450	1150
K_2O Rate, lb/acre	225	225	225	--	225	225	225	--	225	675	225
MgO Rate, lb/acre	173	--	111	--	336	--	214	--	1038	--	663
Nutrient sources	MAP	5-10-15	DAP	--	MAP	5-10-15	DAP	--	MAP	5-10-15	DAP
K_2O sources	KCL Soluble	--	KCl Soluble	--	KCl Soluble	--	KCl Soluble	--	KCl Soluble	--	KCl Soluble
Micronutrients lb/acre:											
Zn, from $ZnSO_4$	7	--	7	--	7	--	7	--	7	--	7
Mn, from MnO	7.2	--	7.2	--	7.2	--	7.2	--	7.2	--	7.2
B, from sodium borate	2.2	--	2.2	--	2.2	--	2.2	--	2.2	--	2.2
Mo, from amm. molyb.	2.0	--	2.0	--	2.0	--	2.0	--	2.0	--	2.0
Seed lb/acre:											
Tall Fescue 31	50	50	50	50	50	50	50	50	50	50	50
Crimson Clover	20	20	20	20	20	20	20	20	20	20	20
White Dutch Clover	6	6	6	6	6	6	6	6	6	6	6
Wood fiber mulch lb/acre	600	600	600	--	600	600	600	600	600	600	600
Curosol gal/acre	45	45	45	--	45	45	45	45	45	45	45

Note: Observations all plots are 1,000 square feet.

except that in those plots the planting cannot be considered satisfactory due to the erosion and the poor coverage. All other plots blended well with the surrounding planting and the coverage was judged satisfactory. No striking difference could be observed between the fertilized plots, although the ones where higher fertilization rates were used looked better.

It was concluded that early establishment of the grass was critical for future appearance and that for that purpose adequate mulching and preparation of the seed bed were more determinant than quality of fertilization.

Longer term effects are still to be observed.

Grassing Experiment No. 2

The planting was made in August 1976. The site was on the shoulders of a heavily travelled two-lane raod near Roswell, Georgia. The shoulders were newly constructed. The soil was typically red clay. The ground was heavily compacted due to heavy traffic over the shoulders. Table 17 describes the fertilizer-seed-mulch formulations used. The large number of controls was necessary because of the very different sun, shade and traffic conditions in the area.

The following observations were recorded.

The site was not adequate for grassing due to the heavy traffic. In four months, the growth in all plots was poor and comparisons difficult. No satisfactory coverage was obtained in any of the plots. While there is a possibility that the grass will recover for future observations in Spring, it appears that the proper recommendation for the planting in the area was not seeding, but sodding.

Table 17. Grassing Experiment No. 2. Formulations.

Plot Number	Approx. Area (ft^2)	Mixture	Nutrient Rates (lb/acre)			Seed Rate (lb/acre)		Mulch Rate (lb/acre)
			N	P_2O_5	K_2O	Bermuda	Tall Fescue	Wood Fiber Cellulose
1	2500	Control[a]	75	225	225	8	40	800
2	2500	HYDROMIX[b]	150	600	225	8	40	800
3	2500	Control	75	225	225	8	40	800
4	500	HYDROMIX	150	600	225	8	40	800
5	2000	HYDROMIX	75	300	225	8	40	800
6	2500	Control	75	225	225	8	40	800
7	2500	HYDROMIX	75	300	225	8	40	800
8	2500	Control	75	225	225	8	40	800
9	2500	HYDROMIX	75	300	225	8	40	800
10	2500	Control	75	225	225	8	40	800
11	2500	HYDROMIX	150	600	225	8	40	800
12	2500	Control	75	225	225	8	40	800
13	2500	HYDROMIX	150	600	225	8	40	800

[a]All controls were fertilized with slurry prepared from 4-112-12.

[b]HYDROMIX formulations were made from MAGOX 98 HR, 13-52-0 and KCl.

Grassing Experiment No. 3

The planting was done in early October, 1976. The sites were right-of-ways along I-85 and along a nearby rural road in the Gwinnett and Hall Counties in Georgia. Similar applications as done previously were conducted, except that hay and asphalt mulch were used to supplement the wood fiber cellulose on some plots. Table 18 describes the treatments used.

Favorable weather followed the grassing. This allowed the grass to start covering the ground in two weeks. However, the areas in which the hay and asphalt were not applied did not show any coverage.

In two months satisfactory stands were observed in all areas and no appreciable difference could be observed between experimental plots and surrounding sites. The areas in which hay and asphalt had not been applied showed some coverage but establishment will be clearly much slower in those plots.

Table 18. Grassing Experiment No. 3. Formulations.

	CONTROLS	EXPERIMENTALS (PLOT NUMBER)						
	0	1	2	3	4	5	6	7*
Plot Size (Approx.)	All surrounding area	0.75 acre	0.5 acre	0.85 acre	0.35 acre	0.65 acre	0.65 acre	0.65 acre
Premix Analysis	(from 34-0-0 and 0-20-20)	7-35-7	6-28-18	12-30-12	8.5-34-8.5	6.7-27-20	6.7-27-20	6.4-32.4-17.2
Nutrient Rates (lb./acre)	52-62-62	50-250-50	60-280-180	46-116-46	190-760-190	50-201-149	50-201-149	100-506-268
Wood Fiber (Cellulose lb. acre)	300	300	300	300	425	300	300	300
Tall Fescue (lb. acre)	50	50	50	50	71	50	50	50
Crimson Clover (lb. acre)	10	10	10	10	28	10	10	10
Mulch Rate								
Hay (tons/acre)	2	not used	not used	2	2	2	not used	not used
Asphalt Emulsion	200	not used	not used	200	200	200	not used	not used

*Mixture for plot 7 was a blend of the following permixed: 750 lb. (6-28-18) 54 lb. (7-35-7)
120 lb. (8.5-34-8.5 80 lb. (6.7-27-20)

CHAPTER VI

FINAL CONCLUSIONS AND RECOMMENDATIONS

Granulation Process and Product

An original process for granulating a fine powdered mixture consisting of sea water magnesia, MAP and other incorporated powders or fines was proven on a pan granulator pilot-plant.

The products, MNP and MNPK, dispensed with drying and cooling, were free-flowing and non-caking, presenting excellent physical properties.

Magnesium ammonium phosphate hexahydrate, a slow-release fertilizer material, was the main component of the granular product. More magnesium ammonium phosphate would be formed after application to the soil.

The product could be dried with removal of about 20% weight loss, thereby generating a higher analysis material without altering substantially the physical properties of the granules. The transformation occurring during drying was the transition from the hexahydrate to the monohydrate.

The products exhibited slow-release characteristics in a leaching column. For example, 20% of the nitrogen from MNP was immediately leachable in the experiment, while this figure was 60% for MAP and only 4% for MAGAMP. For phosphorus the figures were respectively 10%, 55% and 3%. The potassium leachability from MNPK was comparable to that from MAGAMP: about 67% rapidly leachable. The leaching experiments did not consider nitrification factors and the flooding of the columns was only very brief.

The process would require careful control. Granulation of fine powders in a pan granulator requires considerable skills.

The products would have the disadvantage of low $N:P_2O_5$ ratios (1:4 to 1:5, depending on the grade of MAP used).

Field testings were not concluded but the results available thus far indicate that the material is at least as efficient as the common 5-10-15 fertilizer, in a tree fertilization experiment.

Based on the experience obtained in producing and handling the materials MNP and MNPK the following recommendations may be drawn:

(1) The process should be tested in a commercial pan granulator.

(2) All future work as well as future economical feasibility studies should include powdered MAP as feed.

(3) Incorporation of high nitrogen products such as powdered urea or ammonium nitrate would increase the $N:P_2O_5$ ratio of the product and could generate a more appealing grade, while imparting some delayed release characteristics to urea or ammonium nitrate.

(4) Agronomical testing should continue into the MAGAMP market area.

HYDROMIX Method

In conjunction with a grassing operation using hydroseeders a method for producing and using a magnesium ammonium phosphate based slurry fertilizer was developed. The raw materials were sea water magnesia, MAP, KCl and other sources of micronutrients.

The slurry has a low ionic concentration which suggests that it would constitute a safe, non-burning fertilizer.

The insoluble part of the slurry, roughly 70%, proved to be slow-release.

The process provides a premium quality fertilizer from non-premium raw materials through a minimum of processing.

The agronomical testing indicates thus far that the HYDROMIX method is at least equal to ordinary 5-10-15, 4-12-12, ammonium nitrate and 0-20-20 as source of nutrients.

Longer term effects are still to be observed on the plantings performed.

Planting variables such as site preparation and mulch apparently determine more clearly the outcome of the planting than fertilization.

Based on the experience obtained in producing and using HYDROMIX, the following recommendations may be drawn:

(1) Future production and economic feasibility studies should consider powdered MAP as a source of MAP for the process.

(2) Construction of a scaled-down spraying rig should be pursued in order to perform more flexible, economical and adequate testing.

(3) Testing should be extended to include foliar application to food crops.

(4) The possibility of producing slow-release micronutrients from metal ammonium phosphates produced in a similar process as HYDROMIX should be investigated.

APPENDICES

APPENDIX A

ANALYTICAL METHODS FOR THE DETERMINATION OF N, P_2O_5, K_2O and Mg

Introduction

Around 1,000 quantitative chemical analyses were performed during this thesis work. For obvious financial and other reasons it was neither possible nor needed for a commercial laboratory to perform such work. At the same time, official methods of analysis were generally too lengthy and unnecessarily accurate. It was found that fast, economical, unofficial methods existed which were reproducible enough and thus could be calibrated. To the purposes sought they were very proper. Thus, N, K and Mg were analysed by specific ion electrodes. P_2O_5 was analysed by an official spectroscopic method, simplified to some extent. It is acknowledged that the procedures developed are not general and it was not attempted to find the full scope and limitations of the said procedures. In this appendix, basic features of the methods used are presented.

Method for Determination of Nitrogen (15)

This method was used to determine total nitrogen in the leachates obtained when the fertilizer materials MAP, MNP, MNPK, MACAMP and HYDROMIX were subjected to leaching. The method is an ion-selective electrode technique.

It was determined that nitrate nitrogen in the materials listed

above was negligible (16). Thus, it was granted that the total nitrogen was essentially ammoniacal nitrogen. For analysing solids, solutions similar to the leachates would have to be produced from the solids.

Theory of Operation

Ammonium ion and ammonia will exist in equilibrium in water solutions according to the following equation:

$$NH_3 + H^+ \rightleftarrows NH_4^+ \qquad \text{(A-1)}$$

The relative amount of ammonia and ammonium ion is determined by the solution pH. At acid solutions where hydrogen ion is readily available, virtually all the ammonia is converted to ammonium ion. Figure 16 describes the ammonia-ammonium equilibrium as calculated by thermodynamic considerations (15). It is seen that at pH abo 11 the ammonium ion concentration is negligible. Ammonia will be present in solution as a gas. A gas sensing electrode can translate the level of ammonia dissolved as a gas in solution sample in terms of an electrical potential and the electrode response can be related to known ammonium concentrations. The technique is described in detail in the reference given.

In this section, besides the basic knowledge of the process, results from random analyses are compared with results obtained with official methods (17).

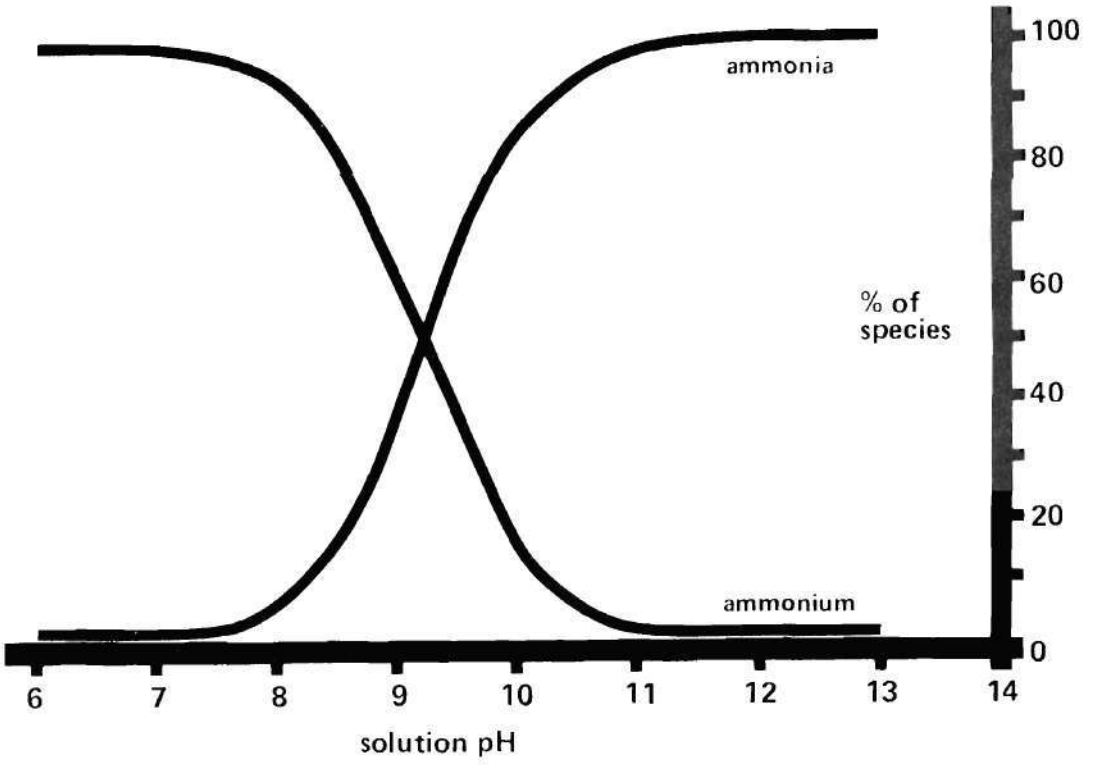

Figure 16. Ammonia-Ammonium Distribution in Solution Versus Solution pH

Official versus Non-official Methods

The following comparisons were made:

Sample	Official Method (17) Percent NH_3	Non-official Method Percent NH_3
1	8.35	8.4
2	7.46	6.75
3	6.7	6.94

It was concluded that the method suited the purpose. Finally, it must be said that pH/ion meters, except those offering a digital reading,

cannot usually be reproducible better than 2%. The comparison given above involves analysis of solids. It may be expected that for very dilute solutions, such as the leachates, the method would work even better.

Method for Determination of Potassium (18)

This method was used to determine total potassium in the leachates solutions obtained when fertilizer materials MAP, MNP, MNPK, MAGAMP and HYDROMIX were subjected to leaching. The method is an ion selective electrode technique.

Fundamentals

An electrical potential develops across a special membrane and an ion exchange resin when solutions containing potassium ions contact the electrode. The electrode response measures the potassium ion activity in the solution. At dilute solutions the activity of an ion is a linear function of its concentration. Thus the electrode response can be related to potassium ion concentrations.

When total ionic strength is greater than 10^{-3} M, other ions interfere with the activity of potassium ions. In this case the ionic strength of the standardizing solutions should be adjusted to $\pm$ 50% of the ionic strength of the sample. The problem is bypassed by using adequate aliquots and sample dilutions.

Official Versus Non-official Methods

The following comparison was made:

Sample	Official (19) Percent K_2O	Unofficial Percent K_2O
1	5.97	6.0
2	6.2	5.5
3	11.49	11.63

It was concluded that the method suited the purposes sought. The same remarks made with respect to the ammonia method are valid.

Method for Determination of Magnesium (20)

This method was used to determine total magnesium in the leachates solutions obtained when fertilizer materials MAP, MNPK, MNPK, MAGAMP and HYDROMIX were subjected to leaching. The method is an ion selective electrode technique.

Fundamentals

The activity of divalent cations Ca^{++}, Mg^{++} in solution can be related to the electrical potential developed across a special membrane and an ion exchange resin in an electrode as this is inserted into the solution. Under proper conditions, the activity of an ion is a linear function of its concentration. Thus concentrations can be measured by the electrode response.

Manufacturer's specifications of raw materials used in the production of the above mentioned fertilizer materials indicate that about 95% of the divalent cations in those materials must be Mg^{++}. Thus most of the divalent cation activity is due to magnesium ion concentration in solution.

Discussion

Since the release of magnesium from all sources analyzed was very slow, it was judged unnecessary to probe the method. It was expected that magnesium, a very insoluble base, would behave like it did on the leaching column.

We note in passing that A.O.A.C. methods were used in the Mg analyses of the solid products (21).

Method for Determination of Total Phosphorus (22)

The method used was an official method for analyzing total phosphorus in fertilizer materials in which all the phosphorus is in the form of orthophosphate. In order to convert all other forms of phosphorus to orthophosphate, several acid hydrolysis methods are recommended (23). It was observed that sample solutions submitted to acid digestion gave the same results as when the preliminary digestion step was not taken. Thus it was concluded that in our samples all phosphate was orthophosphate and that the digestion step was not needed.

Theory of Operation

In dilute solutions orthophosphate ion (PO_4^{-3}) reacts, under acid conditions, with molybdovanadate reagents to form a vanadomolybdophosphoric acid yellow colored complex which exhibits a maximum absorbance at 400 mμ. The absorbance of the complex is measured spectrophotometrically and related to the phosphate concentration.

The method is used for determination of P_2O_5 in all common fertilizer materials (22) as well as in other phosphorus streams (23).

Elimination of the Digestion Step

The acid hydrolysis recommended in some methods (22, 23) was bypassed. This saved a considerable analytical time. The following comparison was made to justify the action:

Sample	Percent Transmittance Persulfate Digestion (23)	Percent Transmittance Non-Digested
1	8.4	8.4
2	7.0	7.0
3	10.5	10.5

It was concluded that all phosphate in the type of fertilizer leachates handled was in the orthophosphate form, which, as a matter of fact, would be expected from MAP downstream products. Thereby the digestion step was not necessary.

We conclude by noting that a small number of the P_2O_5 analyses for solid materials were made using another official method (24).

APPENDIX B

RESULTS FROM THE LEACHING EXPERIMENTS

The tables presented below should be used together with Table 7 and Table 12, given on page 38 and page 60, respectively.

Table 19. Leachability of Granular Products

Column # 1 Material: MNPK (-3/8" + 4 mesh)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K	Mg
1	5.98	2.48	6.1	1.0
2	23.86	12.82	33.8	2.26
3	29.88	16.75	43.8	3.07
4	32.04	18.3	48.0	3.57
5	32.93	19.04	50.5	4.07
6	33.55	19.52	52.2	4.47
7	33.94	19.82	52.4	4.87
8	34.3	19.9	52.5	5.07

Column # 2 Material: MNP (-4 + 6 mesh)

Leacheate (inches of Water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K[a]	Mg
1	1.3	0.77		0.38
2	7.5	6.28		1.52
3	18.66	15.11		2.61

[a]Not applicable.

Column # 2 (Cont'd) Material: MNP (-4 + 6 mesh)

Leacheate (inches of Water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K[a]	Mg
4	21.71	17.73		3.11
5	23.04	19.04		3.41
6	23.84	19.78		3.71
7	24.19	20.18		3.91
8	24.29	20.43		3.95

Column # 3 Material: MNPK (-6 + 8 mesh)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K	Mg
1	11.9	4.93	22.7	1.58
2	27.7	10.85	45.4	4.32
3	34.3	15.25	56.7	4.92
4	35.7	16.09	62.0	5.52
5	36.4	16.57	64.6	6.02
6	37.	17.2	66.1	6.62
7	37.3	17.5	67.4	7.02
8	37.4	17.6	67.9	8.72

Column # 4 Material: MNP (-8 + 12 mesh)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K[a]	Mg
1	2.28	1.95		0.8
2	9.71	7.77		2.78
3	11.19	9.55		3.28
4	12.09	10.05		3.52

[a]Not applicable.

Column # 4 (Cont'd) Material: MNP (-8 + 12 mesh)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K[a]	Mg
5	12.59	10.35		3.91
6	12.94	10.55		4.17
7	13.24	10.77		4.41
8	13.34	10.87		4.51

Column # 5 Material: MNP (-12 + 32 mesh)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K[a]	Mg
1	4.37	3.4		1.5
2	12.2	9.23		3.0
3	14.63	10.58		3.7
4	15.35	10.99		4.3
5	15.53	11.22		4.8
6	15.65	11.42		5.4
7	15.95	11.62		6.1
8	16.01	11.67		6.3

Column # 6 Material: MNP (-32 mesh)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K[a]	Mg
1	32.6	25.0		3.74
2	42.77	31.1		5.25
3	44.47	31.9		6.10
4	45.44	32.3		7.15
5	46.11	32.5		8.32

[a]Not applicable.

Column # 6 (Cont'd) Material: MNP (-32 mesh)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K[a]	Mg
6	46.73	32.7		9.75
7	47.19	32.9		10.57
8	47.48	33.0		11.24

Column # 7 Material: MAGAMP(-6 + 8 mesh)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K	Mg
1	0.77	0.16	18.13	2.89
2	2.07	0.23	35.99	3.93
3	3.42	0.40	48.49	5.54
4	3.92	0.71	58.22	6.47
5	4.24	1.02	61.65	7.2
6	4.47	1.33	4.14	7.71
7	4.6	1.56	65.83	.8
8	4.73	1.76	67.06	7.93

Column # 8 Material: MAP (-8 + 12 mesh)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K[a]	Mg
1	25.59	18.61		
2	49.4	34.35		
3	59.25	44.43		
4	61.73	49.9		
5	62.73	51.75		
6	63.35	52.97		
7	63.67	53.69		
8	63.8	53.96		

[a]Not applicable.

Table 20. Leachability of Slurry Products

Column: $(A_1 + A_2)/2$ Material: HYDROMIX (with MAP)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K	Mg
1	26.28	9.28	29.76	4.79
2	38.37	13.44	38.06	4.79
3	41.21	15.32	41.49	4.79
4	44.16	16.15	44.07	4.79
5	45.21	17.00	45.73	4.90
6	45.68	17.84	46.50	5.02
7	46.11	18.66	47.55	5.21
8	46.23	19.44	47.98	5.36

Column: $(B_1 + B_2)/2$ Material: HYDROMIX (with DAP)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K	Mg
1	37.49	17.87	50.96	9.06
2	46.19	22.70	66.89	9.19
3	.00	24.13	70.94	9.19
4	49.94	24.47	74.07	9.19
5	50.74	24.79	76.21	9.33
6	51.36	25.05	78.20	9.55
7	51.87	25.33	79.09	9.90
8	52.24	25.66	79.93	10.25

Column: $(C_1 + C_2)/2$ Material: HYDROMIX (with powdered MAP)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K	Mg
1	30.49	19.65	33.20	4.79
2	43.63	24.77	37.66	4.92
3	45.42	27.54	39.00	4.93
4	46.47	28.52	41.43	4.94
5	47.48	29.36	43.09	5.16
6	48.57	29.76	43.91	5.36
7	49.05	30.1	44.62	5.64

Column: (D_1) Material: Dry Mix (with MAP)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K	Mg
1	30.49	2.52	50.37	4.79
2	49.94	9.54	58.67	5.39
3	0.62	15.15	66.11	5.53
4	64.82	16.46	67.94	5.53
5	68.50	17.66	69.43	5.62
6	70.31	18.67	70.48	5.76
7	71.79	19.70	70.90	5.91
8	72.80	20.43	71.27	6.13

Column: E_1 Material: Dry Mix (with DAP)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K	Mg
1	29.12	7.87	68.34	6.06
2	44.52	17.27	75.58	6.06
3	52.36	20.50	75.93	6.22
4	56.04	21.72	77.78	6.29
5	58.58	22.27	79.29	6.48

Column: E_1 (Cont'd) Material: Dry Mix (with DAP)

Leacheate (inches of water)	Cumulative Percentage of Nutrient (From initial total) Leached Per Inch of Water			
	N	P	K	Mg
6	60.05	22.71	80.47	6.57
7	61.13	22.76	81.13	6.71
8	61.51		81.62	6.86

APPENDIX C

X-RAY DIFFRACTION METHOD FOR QUALITATIVE ANALYSES OF MISCELLANEOUS PRODUCTS FROM THE GRANULATION AND SLURRY PROCESSES

Introduction

Both granulation and slurry experimental methods yielded fertilizer mixtures. Characterization of such mixtures with respect to identification of main and secondary constituents was necessary for the fundamental knowledge of the processes. X-ray diffraction provided the ideal means for such characterization.

Examination of leaching and drying residues provided multiple insights into the processes and products.

Method

Generalities

The powder diffraction patterns of the samples were compared with the powder diffraction patterns of the standards, i.e., the compounds of which identification was desired. By observing relative intensities of peaks from a sample, together with those of a standard, it was possible to judge if the standard was present in a major way, in a substantial but not major way or in traces or absent from the sample. Some constituents could not be positively identified due to overlapping of their most prominent peaks with peaks of conspicuously present compounds. In such event the presence of those constituents could neither be discarded.

Standards

The standards of interest were collected from the Powder Diffraction File (25). The peaks are presented in Table 21, on page 97.

Apparatus

Fisher Mortar-Grinder.

Phillips Electronic Instruments Type 12215/0 X-Ray Diffractometer.

Norelco Type 42273/1 θ:2θ Goniometer.

Bristol Dynamaster Strip-Chart Recorder.

Procedure

All samples were ground in the mortar-grinder for 45 minutes. Powder Diffraction Patterns were obtained by scanning the samples at a rate of 1° 2θ per minutes, from 5° 2θ to 2θ. Cuk_{α} radiation was used (λ = 1.5405μ). Intensities were measured as peak heights above background and expressed as percent of the strongest line.

Results

The peaks were computed and presented in Table 22, on page 101. A conclusive table is given on page 47 in the text for the granular product, and on page 65 for the slurry products. The charts obtained were photographed and all documentation retained in Project File.

Please refer to the above mentioned pages for the proper discussion of the results.

Table 21. Standard Tabulated Powder Diffraction Patterns

MgO		$Mg(OH)_2$		$MH_4H_2PO_4$	
d(Å)	I/I_o(%)	d(Å)	I/I_o(%)	d(Å)	I/I_o(%)
2.431	10	4.77	90	5.32	100
2.106	100	2.365	100	3.75	65
1.489	52	1.794	55	3.07	90
1.270	4	1.573	35	3.06	75
1.216	12	1.494	18	2.659	18
1.0533	5	1.373	16	2.651	16
0.9412	17	1.310	12	2.009	30
0.8600	15	1.183	10	2.004	20
0.8109	3			1.602	10
		All others $\leq$ 10		All others $\leq$ 10	

$Mg_3(PO_4)_2 \cdot 4H_2O$		$Mg_3(PO_4)_2 \cdot 3H_2O$		$Mg\ HPO_4 \cdot 3H_2O$	
6.1	20	8.04	18	5.34	100
5.2	80	6.96	100	4.71	60
4.10	100	3.02	10	3.46	40
3.23	80	2.94	25	5.94	30
3.09	60	2.81	14	All others $\leq$	10
2.87	40	2.59	10		
2.73	40	2.41	12		
2.65	80	2.13	10		
2.51	40	All others $\leq$10			
2.34	40				
1.91	20				
1.79	20				
1.74	20				
All others $\leq$ 10					

Table 21 (Continued). Standard Tabulated Powder Diffraction Patterns

$MgHPO_4 \cdot 7H_2O$		$Mg(H_2PO_4)_2$		$(NH_4)_2HPO_4$	
d(Å)	I/I_o(%)	d(Å)	I/I_o(%)	d(Å)	I/I_o(%)
6.56	50	4.95	16	5.57	75
5.42	50	4.47	60	5.05	100
4.90	5	4.08	50	4.99	10
4.55	90	3.75	12	4.94	65
4.42	90	3.60	20	4.13	40
4.13	90	3.37	80	4.03	20
4.02	90	3.14	100	4.00	30
3.63	60	2.98	60	3.78	50
3.29	100	2.64	28	3.67	10
3.03	60	2.55	24	3.43	20
2.82	100	2.33	70	3.37	20
2.704	90	2.24	16	3.22	65
2.627	90	2.16	4	3.19	10
2.397	60	2.03	4	3.14	45
2.280	60	2.19	24	3.06	45
2.225	60	1.84	4	3.04	14
2.067	70	1.72	12	2.820	25
1.991	90	1.64	8	2.799	30
1.875	60	1.56	12	2.542	35
1.818	60	1.4	12	2.471	16
1.735	60	1.36	4	2.435	10
1.653	60	1.32	8	2.300	14
1.585	60	1.27	4	2.079	10
1.551	60	1.20	8	2.017	14
1.492	50	1.16	8	2.005	10
1.450	50	1.13	4	1.915	14
1.399	50			1.700	12
1.317	60			All others $\leq$	10

Table 21 (Continued). Standard Tabulated Powder Diffraction Patterns

$Mg_2P_2O_7$		$Mg_2P_2O_7$		$NH_4MgPO_4 \cdot H_2O$	
d(Å)	I/I_o(%)	d(Å)	I/I_o(%)	d(Å)	I/I_o(%)
4.19	20	4.14	20	8.77	100
3.02	100	3.015	100	4.72	30
2.93	35	2.976	55	4.20	25
2.55	9	2.528	14	2.92	40
2.10	11	2.415	12	2.80	50
1.87	8	2.105	16	2.50	20
1.83	8	1.855	8	2.28	10
1.72	4	1.574	10	1.674	10
1.68	3	All others $\leq$ 5		All others < 10	
1.59	16	(Heated $MgNH_4PO_4$			
1.48	5	at 900° - cooled			
1.39	6	20° C)			
(Hi temp inv.					
250°C 68 ± 2°C)					

KCl	
d(Å)	I/I_o(%)
3.145	100
2.224	69
1.816	23
1.573	8
1.407	20
1.25	13
1.1126	2
1.0490	6
0.9951	2
0.9486	3
0.9083	1
0.8727	2

$Mg(PO_4)_2$	
d(Å)	I/I_o(%)
4.31	40
4.12	40
4.08	60
3.85	80[d]
3.66	60
3.44	100
2.993	40
2.532	40
2.497	60
2.414	60[d]
2.125	40[d]
2.040	40
1.774	60[d]
1.692	40
1.691	40

[d] Refers to doublet.

Table 21 (Continued). Standard Tabulated Powder Diffraction Patterns

$MgNH_4PO_4 \cdot 6H_2O$		$MgKPO_4 \cdot 6H_2O$		NH_4Cl	
d(Å)	I/I_o(%)	d(Å)	I/I_o(%)	d(Å)	I/I_o(%)
5.905	40	5.54	80	3.87	25
5.601	60	5.37	35	2.74	100
5.378	25	4.23	100	2.238	4
4.257	100	4.12	100	1.939	8
4.139	40	3.25	50	1.733	6
3.475	12	2.97	30	1.582	25
3.280	25	2.90	50	1.370	6
3.022	14	2.77	90	1.292	4
2.958	25	2.69	95	1.225	6
2.919	55	2.64	40	1.1687	4
2.802	35	All others $\leq$	20	1.1188	2
2.722	16			1.0751	2
2.690	50			1.0357	4
2.660	45			0.9680	2
2.352	12			0.9400	2
2.054	12			.9134	4
2.014	10			.8890	2
1.960	14			.8667	2
All others $\leq$	10			.8457	4
				.8263	4
				.7911	4

Table 22. X-Ray Powder Diffraction Patterns Obtained for Several Experimental Products, Both Slurry and Granular, and for Commercial MAGAMP

G-1		G-4		G-4 (Continued)	
d(Å)	I/I_o(%)	d(Å)	I/I_o(%)	d(Å)	I/I_o(%)
8.70	30	5.86	60	2.31	5
7.72	5	5.75	15	2.24	5
6.10	8	5.57	72	2.17	6
5.86	33	5.34	28	2.10	22
5.57	73	5.15	42	2.05	7
5.35	16	5.03	15	2.01	11
4.72	13	4.92	10	1.98	5
4.57	8	4.72	5	1.96	11
4.24	100	4.57	5	1.92	5
4.12	43	4.46	4	1.87	7
3.77	24	4.39	5	1.79	11
3.72	14	4.29	32	1.76	8
3.46	9	4.23	100	1.74	12
3.28	27	4.11	41	1.71	6
3.04	18	3.98	7	1.68	5
2.95	20	3.88	16		
2.91	48	3.57	10		
2.79	64	3.45	30		
2.78	10	3.35	15		
2.68	51	3.28	25		
2.65	44	3.21	11		
2.50	9	3.13	14		
2.39	6	3.04	15		
2.34	12	3.01	34		
2.25	4	2.95	31		
2.19	9	2.91	54		
2.16	5	2.79	52		
2.12	6	2.71	13		
2.05	12	2.68	44		
2.01	9	2.65	37		
1.96	11	2.58	15		
1.92	5	2.53	9		
1.87	5	2.51	9		
1.80	10	2.45	7		
1.76	8	2.39	8		
1.73	9	2.34	13		
1.68	5				
1.65	4	(cont. above)			

G-6

d(Å)	I/I_o(%)
6.06	6
5.86	40
5.57	67
5.34	24
5.15	6
5.03	7
4.57	5
4.23	100
4.11	40
4.02	4
3.98	4
3.75	4
3.45	13
3.28	25
3.15	26
3.13	73
3.01	18
2.95	20
2.91	57
2.79	40
2.73	13
2.71	12
2.68	47
2.65	35
2.53	5
2.51	6
2.38	5
2.34	11
2.24	13
2.22	17
2.13	7
2.10	9
2.05	7
2.01	10
1.95	3
1.96	10
1.92	3
1.87	5
1.80	8
1.76	8
1.74	12
1.71	5
1.68	5
1.65	4

G-7

d(Å)	I/I_o(%)
6.06	5
5.86	34
5.57	54
5.34	24
4.57	7
4.23	100
4.11	36
3.58	3
3.45	10
3.28	25
3.01	11
2.95	18
2.91	48
2.79	33
2.71	10
2.68	43
2.65	35
2.50	7
2.38	2
2.34	11
2.25	4
2.17	4
2.12	7
2.10	7
2.05	8
2.01	8
1.98	3
1.96	11
1.92	3
1.87	3
1.84	3
1.80	9
1.79	9
1.76	8
1.73	12
1.71	4
1.68	2
1.65	3
1.59	4

G-8

d(Å)	I/I_o(%)
6.06	7
5.86	36
5.57	59
5.34	24
4.57	5
4.23	100
4.11	37
3.53	5
3.45	12
3.28	26
3.02	13
2.95	17
2.92	53
2.79	35
2.71	9
2.68	47
2.65	36
2.54	3
2.51	7
2.39	3
2.34	10
2.25	2
2.17	2
2.15	2
2.12	4
2.10	4
2.05	8
2.01	9
1.98	7
1.96	11
1.92	3
1.87	6
1.84	3
1.80	10
1.76	8
1.73	12
1.71	5
1.68	5

G-10		S-1		S-4	
d(Å)	I/I_o(%)	d(Å)	I/I_o(%)	d(Å)	I/I_o(%)
8.67	100	6.06	3	6.06	12
5.27	9	5.82	17	5.82	17
4.72	44	5.53	100	5.53	93
4.21	44	5.34	21	5.34	55
3.74	6	4.55	3	4.57	6
3.64	8	4.23	70	4.23	100
3.45	2	4.11	35	4.11	73
3.36	3	3.53	3	3.53	5
3.23	4	3.45	4	3.45	5
3.07	7	3.28	24	3.28	27
2.92	13	3.17	2	3.17	3
2.80	92	3.01	7	3.06	7
2.49	10	2.94	11	3.01	7
2.40	13	2.90	28	2.94	28
2.33	10	2.79	49	2.90	29
2.27	9	2.70	7	2.79	56
2.12	15	2.68	40	2.71	15
2.00	2	2.65	22	2.68	98
1.86	4	2.53	3	2.65	30
1.85	4	2.50	4	2.53	4
1.82	4	2.38	3	2.50	9
1.76	4	2.34	7	2.38	5
1.76	3	2.24	2	2.34	8
1.73	2	2.17	2	2.24	3
1.72	2	2.12	4	2.17	1
1.67	5	2.07	3	2.12	5
1.62	7	2.05	6	2.06	4
		2.01	8	2.05	7
		1.98	3	2.01	11
		1.96	7	1.98	5
		1.92	3	1.96	12
		1.86	3	1.92	8
		1.84	2	1.86	3
		1.80	8	1.84	3
		1.79	7	1.80	13
		1.76	5	1.79	16
		1.73	7	1.76	11
		1.71	3	1.73	10
		1.68	2	1.71	3
		1.65	2	1.68	5
		1.59	4	1.59	6
		1.58	5	1.58	6

APPENDIX D

X-RAY DIFFRACTION METHOD FOR QUANTITATIVE ANALYSIS OF $MgNH_4PO_4 \cdot 6H_2O$ IN A TYPICAL MNP PRODUCT

Introduction

In order to characterize the granular mixture which was the subject of this writing, the extent of the reaction

$$MgO + NH_4H_2PO_4 + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \qquad (D\text{-}1)$$

had to be determined. Qualitative x-ray examination indicated that most if not all magnesium ammonium phosphate is in the hexahydrate form. Thus conversion of the reactants in the granulation process can be measured by the quantitative analysis of $MgNH_4PO_4 \cdot 6H_2O$ in the granular product. A typical MNP product (-4+6 mesh) was chosen for the analysis. This product had 2.78% free moisture and showed a 23.01% weight loss @ 105°C.

Method

The method used is known as the Internal Standard Technique (26). The internal standard was chosen to be WO_3, tungsten trioxide, orthorhombic. The peak in WO_3 chosen was a (200) peak showing a 95% relative intensity at a d-spacing of 3.69 Å. The $MgNH_4PO_4 \cdot 6H_2O$ peak chosen was a (130) peak displaying 25% intensity at a d-spacing of 3.28 Å.

Apparatus

Fisher Mortar-Grinder.

Burton Clinical Shaker.

Analytical Balance.

Phillips Electronic Instruments Type 12215/0 X-Ray Diffractometer with Norelco Type 42273/1 θ:2θ Goniometer.

Ortec System 400/700 Amplifiers and Counters.

Brystol Dynamaster Strip-Chart Recorder.

Reagents

Magnesium Oxide, U.S.P.--Light, Merck.

Ammonium Phosphate, dibasic, Fisher Scientific Co.

Hydrochloric Acid, dilute solution.

Procedure

$MgNH_4PO_4 \cdot 6H_2O$ was prepared by dissolving MgO in weak acid solution and precipitating the magnesium phosphate when the first solution reacted with a $(NH_4)_2HPO_4$ saturated solution. The precipitate was filtered, washed and the cake was dried in vacuum. X-ray examination of the cake after drying showed that it consisted of pure $MgNH_4PO_4 \cdot 6H_2O$.

All the materials were ground in the mortar-grinder for 45 minutes. 0.200 g of WO_3 were mixed with 1.000 g of pure $MgNH_4PO_4 \cdot 6H_2O$ to produce the "standard." 0.200 g of WO_3 were mixed with 1.000 g of sample MNP to produce the "sample." The mixtures were shaken for one hour in the clinical shaker to assure uniformity.

The selected peaks were scanned at the rate of 1/8° 2θ per minute, using the Ortec System 400/700 peak analyzers to record the number of x-rays detected. The WO_3 peak was scanned from 26.800° 2θ to 24.675° 2θ. The $MgNH_4PO_4 \cdot 6H_2O$ peak was scanned from 26.800° 2θ to 27.3000° 2θ. Radiation source was Cu k_α (λ = 1.5405μ).

Results

The following data were generated:

Material		Radiation Counts WO_3 Peak	Radiation Counts $MgNH_4PO_4 \cdot 6H_2O$ Peak
Standard	Total	101,519	32,160
	Background	11,559.5	7,621
	Net	89,959.5	24,539
Sample	Total	102,216	23,301
	Background	15,512	10,063.5
	Net	86,704	13,237.5

The weight percentage of $MgNH_4PO_4 \cdot 6H_2O$ in sample was calculated as follows.

The ratio of $MgNH_4PO_4 \cdot 6H_2O$ counts to WO_3 counts was, in the standard, 0.27278 and in the sample, 0.15267. Then from the 100% $MgNH_4PO_4 \cdot 6H_2O$ ratio, the percentage-ratio relationship was calculated to be:

$$\frac{100}{0.27278} = 366.5981$$

From this figure the percentage of $MgNH_4PO_4 \cdot 6H_2O$ in the sample was calculated to be:

$$366.5981 \times 0.15267 = 55.97\% \text{ in weight}$$

The statistical or counting error was calculated as follows:

$$\% \text{ error} = 0.675/N$$

where N is the total number of x-ray counts. Thus, it was found:

		% Error
Standard	$MgNH_4PO_4 \cdot 6H_2O$ Peak	0.431
Standard	WO_3 peak	0.225
Sample	$MgNH_4PO_4 \cdot 6H_2O$ Peak	0.587
Sample	WO_3 Peak	0.229
	Total Counting Error	± 1.6%

Based on an accuracy of ± 0.001 g on each measurement, the sample preparation weighing error was estimated to be ± 1.20%[3]. The calculations above indicate that the total error in the analysis performed was less than 3%. Experience shows that such errors are more likely in the neighborhood of 5%. For a discussion of the results obtained, please refer to the text on pages 46-48.

APPENDIX E

METHOD FOR CALCULATION THE CONVERSION OF MAGNESIA AND MONOAMMONIUM PHOSPHATE TO MAGNESIUM AMMONIUM PHOSPHATE HEXAHYDRATE IN THE PAN GRANULATION PROCESS

Introduction

The determination of $MgNH_4PO_4 \cdot 6H_2O$ content in the MNP granular product by X-ray diffraction (internal standard technique showed 55.9 weight percent of that compound in the samples submitted for analysis). At the same time, qualitative X-ray diffraction examinations showed that virtually all of the magnesium ammonium phosphate in MNP wa produced was the hexahydrate. On the other hand, examination of dried product (dried at 105° C) indicated that dried material consisted almost totally of magnesium ammonium phosphate monohydrate. That is to say that the weight loss under those conditions corresponds to the loss of free water and of water from the transition from the hexahydrage to the monohydrate:

$$MgNH_4PO_4 \cdot 6H_2O \xrightarrow[57\,^{\circ}C]{} MgNH_4PO_4 \cdot H_2O + 5H_2O \qquad \text{(E-1)}$$

Consequently it was assumed to be possible to calculate the amount of $MgNH_4PO_4 \cdot 6H_2O$ in MNP granules solely from the free moisture data and the weight loss @ 105°C data. This method would be obviously more simple and economical than the powder diffraction technique.

Determination of Free Water (10)

An official method used to determine free water (not including water of crystallization) was employed. The method is based on the fact that absorbed water is removed from fertilizers when held under vacuum and in close proximity to a strong dehydrating agent such as magnesium perchlorate, phosphorus pentoxide or barium oxide. A finely ground fertilizer sample of known weight is placed in a vacuum desiccator in which one of the above dehydrating agents are also present. A 520-570 mm Hg vacuum is pumped and the desiccator sealed. In 16-18 hours the sample is weighed and the weight loss recorded as free moisture. Incidentally, it was found that the free moisture content of almost all MNP and MNPK cured materials was 2% or less.

Determination of "Total" Moisture (27)

The method for accounting the weight loss at 105°C as total moisture was found to be not applicable in the case of magnesium ammonium phosphate. It was already explained that such loss corresponded to the free moisture plus five of the six molecules of the water in the hexahydrate.

Calculation of the Conversion of MgO and $NH_4H_2PO_4$ to $MgNH_4PO_4 \cdot 6H_2O$

The reactants sea water magnesia and MAP are impure chemicals. Based on manufacturer's specifications, it may be assumed that a feed consisting of such raw materials would contain 8% impurities and 2% moisture. Based on such figures plus the assumption that all the water lost by MNP @ 105 was part of the water of crystallization plus free water, the actual fraction of the reactants in the feed converted to

magnesium ammonium phosphate may then be calculated.

The conversion of the feed to the product may be defined as the extent of the reaction

$$MgO + NH_4H_2PO_4 + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \qquad (E-2)$$

From reaction (E-1) it can be written:

$$M6 = \frac{245.43 \times M}{90}$$

where 245.43 is the molecular weight of $MgNH_4PO_4 \cdot 6H_2O$,

90 is the weight of 5 mols of water in grams,

M is the weight loss @ 105°C minus free water,

and M6 is the mass of the hexahydrate in the original sample.

Therefore the conversion of the reaction (E-2) can be calculated by the following formula:

$$\%C = \frac{M6 \times 155.35 \times 100}{245.43 \times 0.9 \times IT}$$

where 155.35 is the molecular weight of the monohydrate,

IT is the initial mass of the sample,

and 0.9 is a factor which corrects for the level of impurities and moisture in the raw materials.

Following the assumption that the free water in MNP and MNPK materials stands around 2%, our calculations can be simplified so that the percentual conversion of reaction (E-2) can be calculated directly from the percent weight loss at 105°C data. Upon performing such calculations, Figure 17 was obtained.

Discussion

Figure 16 can be used to estimate the conversion in MNP materials, if for patent purposes it is desirable to keep the conversion in plant below 50%.

The method described is accurate to characterize the MNPK products. For example, X-ray quantitative techniques indicated 55.9% $MgNH_4PO_4 \cdot 6H_2O$ in a typical MNP product. Using Figure 17 and the weight loss at 105°C for that sample (23.08%) it is found about 55% $MgNH_4PO_4 \cdot 6H_2O$ in that material.

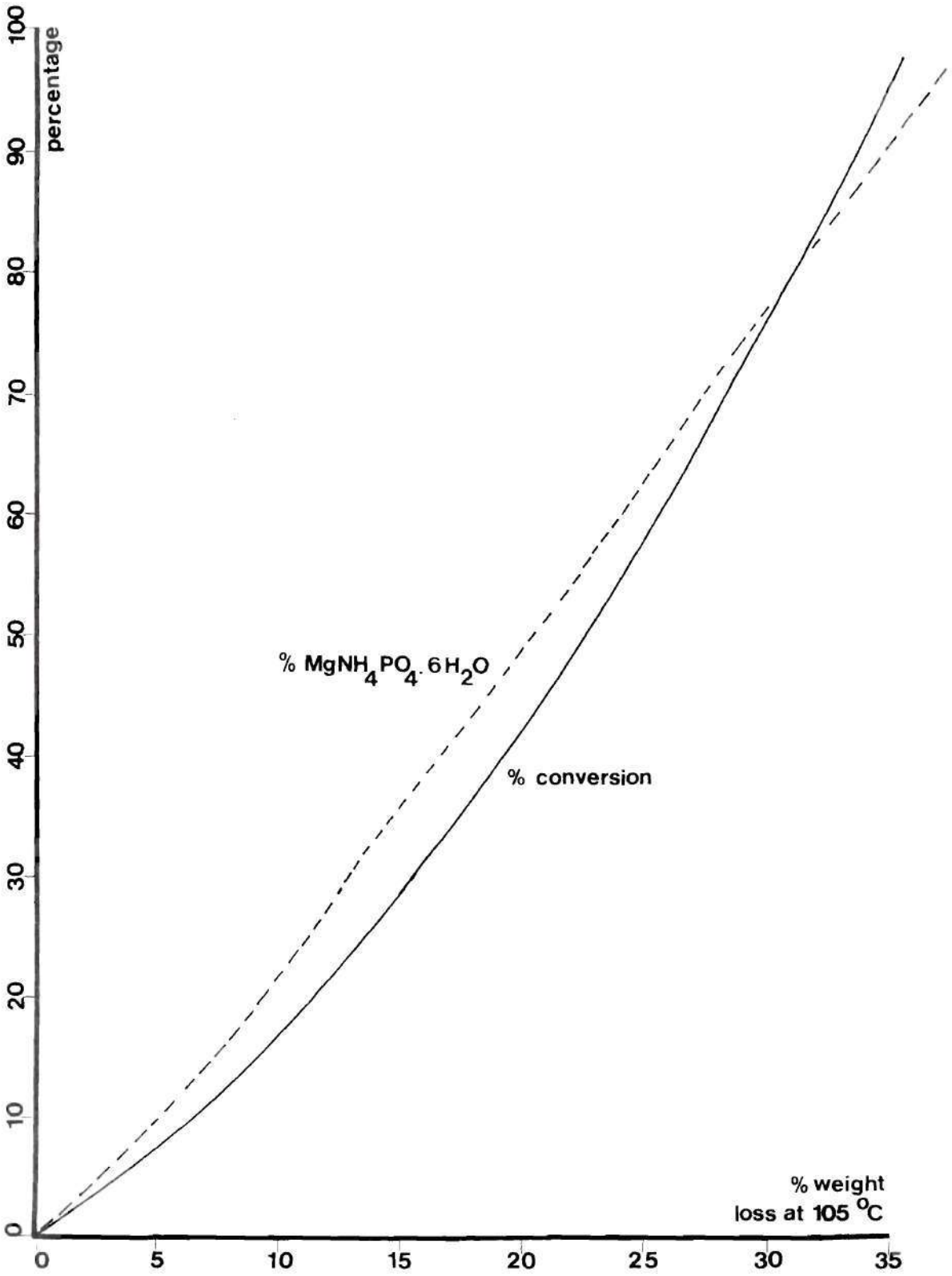

Figure 17. Percent Conversion of Magnesia and Monoammonium Phosphate to Magnesium Ammonium Phosphate Hexahydrate Versus Water of Granulation.

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VITA

The author was born on January 31, 1949, in Hong Kong, China. In 1951, his parents moved to Brazil, where he was raised, received formal education and eventually constituted his own family.

He is a graduate from the School of Engineering of the UFRGS (Federal University of the State of Rio Grande do Sul), in Brazil, having been chosen by his 1970 classmates to be valedictorian. He was also a vice-president of the school's student union. After receiving the Chemical Engineering degree, he was responsible for a mining operation in Southern Brazil. During the same period he has founded and helped in the initial organization of what is today Momentum Engenharia Ltda., a small but well recognized engineering company in the State of Rio Grande do Sul.

In July of 1973 he had the opportunity of visiting the United States of America. He was invited for a training visit with TVA-NFDC (Tennessee Valley Authority--National Fertilizer Development Center). During that visit he has decided to pursue advanced education in this country. He is a M. Sc. in Chemical Engineering from Georgia Tech (1975).

At Tech he has served at the Graduate Senate during the 1975-1976 academic year and he has been for the last three years a produce buyer and a job organizer for the Together Food Co-op. He is also a volleyball player at the Georgia Tech Volleyball Club.

Last but not least, he was married in 1972 to the former Maria Elisa Alfonso Duarte and they are the parents of Mariana and Iara.